

The Origin of Marginal Compositional Reversals in Basic–Ultrabasic Sills and Layered Intrusions by Soret Fractionation

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Marginal reversals—a common feature of many basic differentiated igneous bodies regardless of their size and bulk composition—are remarkable in being a mirror of the Layered Series. These are distinguished by: (1) an apparent lack of mass balance between the lower part of the marginal reversals, including chilled margins, and the bulk composition of the intrusions; (2) mineral crystallization sequences and (3) mineral compositional trends, which are both essentially the opposite of those in the Layered Series; (4) the cotectic composition of rocks composing the marginal reversals; (5) the capacity to form from both phenocryst-rich and phenocryst-free parental magmas; (6) the capability to develop along the floor, subvertical walls and even the roof of magma chambers. None of the current models of magma chamber evolution can provide an adequate explanation for the characteristic features of the marginal reversals. The problem can be resolved in the context of a model combining Soret diffusion in thin liquid boundary layers at the magma chamber margins and vigorous convection in the main magma body. The key proposal is that the formation of marginal reversals takes place through the non-equilibrium evolution of liquid boundary layers as a result of a temperature gradient imposed by the cold country rock. The fundamental explanation for the mirror image of a marginal reversal is that the non-equilibrium Soret fractionation works in a manner opposite to that of the equilibrium crystal–liquid fractionation that produces the Layered Series.

KEY WORDS: *marginal compositional reversals; sills; layered intrusions; Soret fractionation*

INTRODUCTION

Much of our present understanding of the fractional crystallization history of basaltic magmas is derived from the record of crystallization preserved in unique natural laboratories—basic–ultrabasic sills and layered intrusions. A remarkable and common feature of many basic–ultrabasic sills (e.g. Gunn, 1966; Simkin, 1967; Froelich & Gottfried, 1988) and layered intrusions (e.g. Campbell, 1978; Irvine, 1980; Alapieti, 1982; Wilson & Engell-Sørensen, 1986) is the presence of marginal compositional reversals. These also occur in some lavas and lava lakes (e.g. Moore & Evans, 1967; Bédard, 1987; Helz *et al.*, 1989). An enigmatic feature of marginal compositional reversals is that in terms of modal, phase and cryptic layering they represent a mirror image of the Layered Series. It appears that magma in the sills and layered intrusions crystallized concurrently upward and downward to produce the same rock sequences. Unsuccessful attempts to explain this apparent paradox in terms of conventional mechanisms of magma differentiation (e.g. crystal settling, multiple magma injection, flow differentiation, compositionally zoned magma, *in situ* crystallization) led me to pay attention to a currently unpopular mechanism of magma differentiation combining Soret diffusion in thin liquid boundary layers at the chamber margins and vigorous convection in the main magma body (Shaw *et al.*, 1976; Hildreth, 1977, 1979, 1981; Spera, 1977; Hess, 1989; Wilson, 1993). This mechanism, evidence for which is provided by a new interpretation of the character of Soret fractionation in

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natural near-liquidus magmas, is found to provide an adequate explanation for most marginal compositional reversals. Deciphering their origin provides new insights into the mechanisms of magma differentiation in crustal magma chambers, which is of great importance for understanding the processes responsible for the formation of different compositional profiles in basic–ultrabasic sills (Latypov, 2003).

MARGINAL COMPOSITIONAL REVERSALS IN SILLS AND LAYERED INTRUSIONS

There are six distinctive features of marginal compositional reversals in basic–ultrabasic sills and layered intrusions that impose strict constraints on any model for their formation. These are: (1) an apparent lack of mass balance between the lower part of the marginal reversals, including the chilled margins, and the bulk composition of the intrusions; (2) phase crystallization sequences and (3) mineral compositional trends that are the inverse of those in the Layered Series; (4) the cotectic composition of rocks composing the marginal reversals; (5) the capacity to form from both phenocryst-rich and phenocryst-free parental magmas; (6) the capability to develop along the floor, subvertical walls and even the roof of magma chambers.

To illustrate the first four distinctive features, compositional reversals that are developed at the base of the 1700 m thick Monchegorsk layered intrusion, Kola Peninsula, the ~85 m thick Kharayelakh sill and the 50 m thick Noril'sk-I sill, Noril'sk region, Russia, are shown in Figs 1–3 and briefly discussed in the text and figure captions. Detailed information on the petrography, geochemistry and petrology of the Monchegorsk intrusion (e.g. Dokuchaeva & Yakovlev, 1994; Sharkov & Smolkin, 1998) and the Noril'sk intrusions (e.g. Czamanske *et al.*, 1994, 1995; Zen'ko & Czamanske, 1994; Krivolutskaya *et al.*, 2001) can be found elsewhere. The last feature is illustrated by generalized sections across the Jemberlana intrusion (Campbell, 1978) and the Muskox intrusion (Irvine & Smith, 1967) in Fig. 4. The distinctive features of marginal reversals are discussed in more detail below.

Lack of mass balance

It is generally accepted that chilled margins will form rather rapidly for a magmatic body emplaced into relatively cold country rock. Such chilled margins are often considered to provide a reliable indicator of the parental magma composition. Nearly all gravitational

settling and *in situ* crystallization models explaining the nature of the so-called S-shaped vertical profile (Fig. 5a; Marsh, 1996) are implicitly based on this assumption. In reality, however, natural examples exhibiting similarity between the composition of chilled margins and the bulk of intrusions are very rare. Among them one can include the Kilauea Iki lava lake, Hawaii (Helz *et al.*, 1989) and the Vavukanskii basic sill, Siberia (Frenkel' *et al.*, 1988). The preponderance of data on sills and layered intrusions indicates that this basic assumption is commonly incorrect, as the composition of the chilled margins is generally far from the bulk composition of the intrusions. Simkin (1967) presented detailed vertical variations in modal olivine content through the sills of the island of the Skye, Scotland, clearly indicating that their bulk compositions contained 2.5–6 times the amount of olivine present in and near the chilled margin. Froelich & Gottfried (1988), in particular, emphasized that none of the high-TiO₂ diabase sheets in the Culpeper basin, North America, exhibited mass balance between the bulk of the intrusions and the chilled margins in any given section across the exposed tilted sheets or through those penetrated by drill cores. Upton & Wadsworth (1967) documented that the bulk composition of a sill in the island of Reunion, Indian Ocean, is considerably more basic than the mugearite that forms the chilled contacts. The same discrepancy between the composition of the bulk intrusion and the chilled margin has been reported by Hamilton (1965) and Gunn (1966) for many tholeiitic sills and sheets in Antarctica. A rather evolved composition of the basal contact gabbrodolerite, which is not correlated with the average composition of the intrusions, is a long-standing problem for all the ore-bearing intrusions of the Noril'sk region, Russia (Ryabov, 1992; Czamanske *et al.*, 1994, 1995; Zen'ko & Czamanske, 1994). The same discrepancy holds for most basic–ultrabasic layered intrusions, although this is commonly overlooked because of the absence of either chilled margins or complete rock sequences or both. Figures 1–3 display an apparent lack of mass balance between the bulk of the three intrusions and their lower parts, comprising basal zones and chilled margins, in terms of the average bulk-rock MgO content and mg-number (or olivine Fo) ratio. Some additional examples of sills with the same lack of compositional balance are presented in a companion paper (Latypov, 2003). The shape of the ideal overall trend of differentiation shown in Fig. 5a, therefore, is far from the compositional profiles of most sills and layered intrusions. The trend illustrated in Fig. 5b seems to be much more consistent with natural observations and must be explained by any model of magma differentiation.

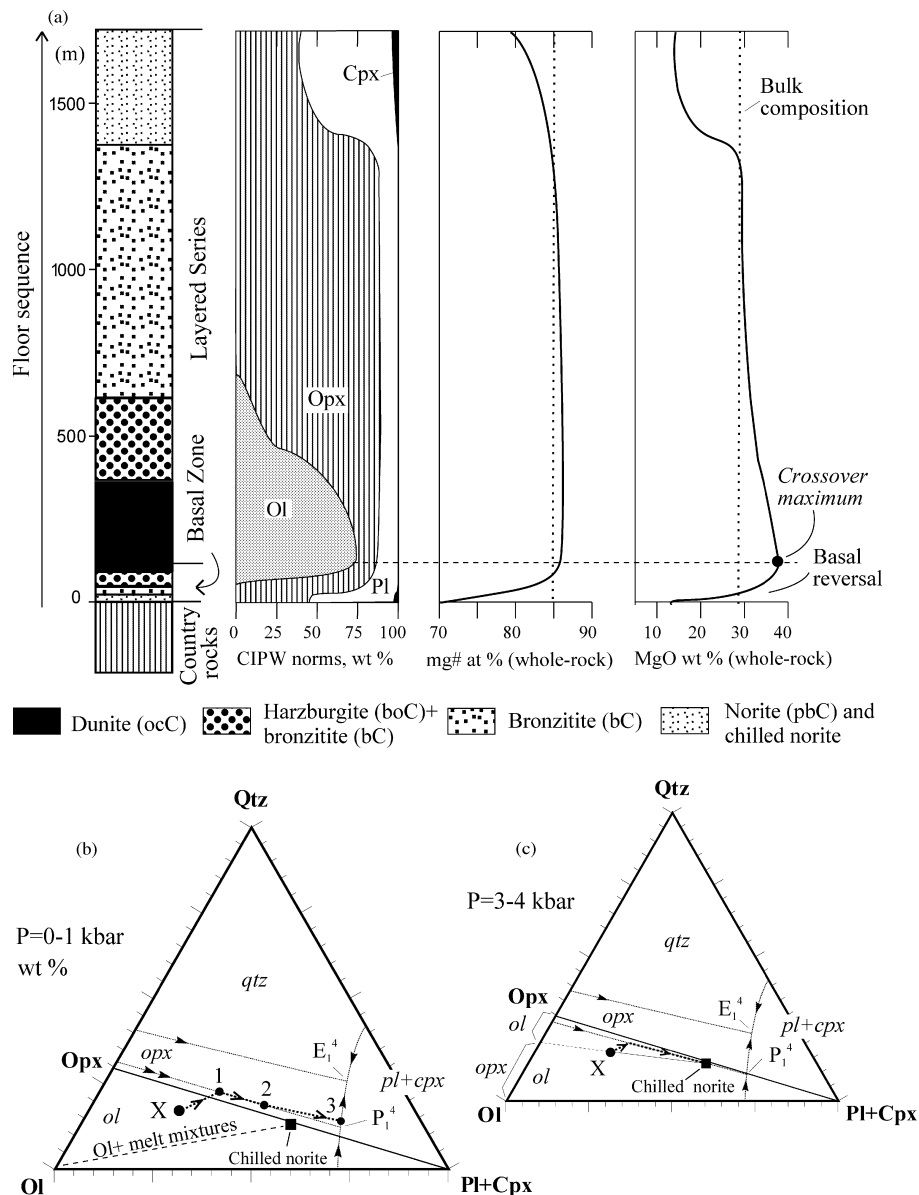


Fig. 1. (a) Generalized stratigraphic section through the Monchegorsk layered intrusion (Kola Peninsula, Russia), showing variation in CIPW normative mineralogy and in whole-rock mg-number and MgO with stratigraphic height. The floor sequence of the intrusion comprises the Basal Zone and the Layered Series. The line of demarcation between the units comprising the floor sequence runs through the crossover maxima exhibiting the most primitive rock composition in the entire section of the intrusion. The upper chilled margin is eroded. The compositional profiles through the Layered Series are based on the author's original unpublished data and those through the Basal Zone on data from Sharkov (1980) and Dokuchaeva & Yakovlev (1994). The Basal Zone of the intrusion exhibits a compositional reversal characterized by: (i) an inverse order of phase crystallization $Pl + Opx \rightarrow Opx \rightarrow Opx + Ol \rightarrow Ol$; (ii) a strong difference in mg-number and lack in mass balance in MgO between the lower part of the Basal Zone and bulk composition of the intrusion; (iii) basal MgO and mg-number enrichment trends. (b) A phase diagram $Ol-(Pl + Cpx)-Qtz$ at 0-1 kbar displays the differentiation trend of the initial parental magma composition $X [Ol + L (X-1) \rightarrow Ol + Opx + L (1-2) \rightarrow Opx + L (2-3) \rightarrow Opx + Pl + L (3)]$ consistent with the cumulus phase sequence in the overlying Layered Series. The great difference in composition of the chilled norite and the bulk composition of the intrusion is evident from the phase diagram. The line connecting chilled norite with the Ol apex shows the range of rock compositions that can be produced from mixtures of a noritic liquid with olivine phenocrysts in the frame of a crystal settling model. (c) A phase diagram $Ol-(Pl + Cpx)-Qtz$ at 3-4 kbar shows a possible way to derive a noritic liquid by differentiation of parental magma X along a cotectic line $Ol + Opx + L$ during its ascent towards the surface. Such a noritic liquid is in equilibrium with olivine and orthopyroxene, with orthopyroxene/olivine ratio being close to 2:1 as defined by an intersection of an extension of the line X -chilled norite with the conode $Ol-Opx$. E_1^4 , $Qtz + Pl + Opx + Cpx = L$; P_1^4 , $Opx + Pl + Cpx = Ol + L$; mg-number = $100Mg/(Mg + Fe^{2+} + Fe^{3+})$. Hereafter: E , eutectic point; P , peritectic point; L , melt. Superscripts indicate the number of components involved in the given equilibrium, and subscripts show the number of this equilibrium in the system. Phase diagrams from Dubrovskii (1998).

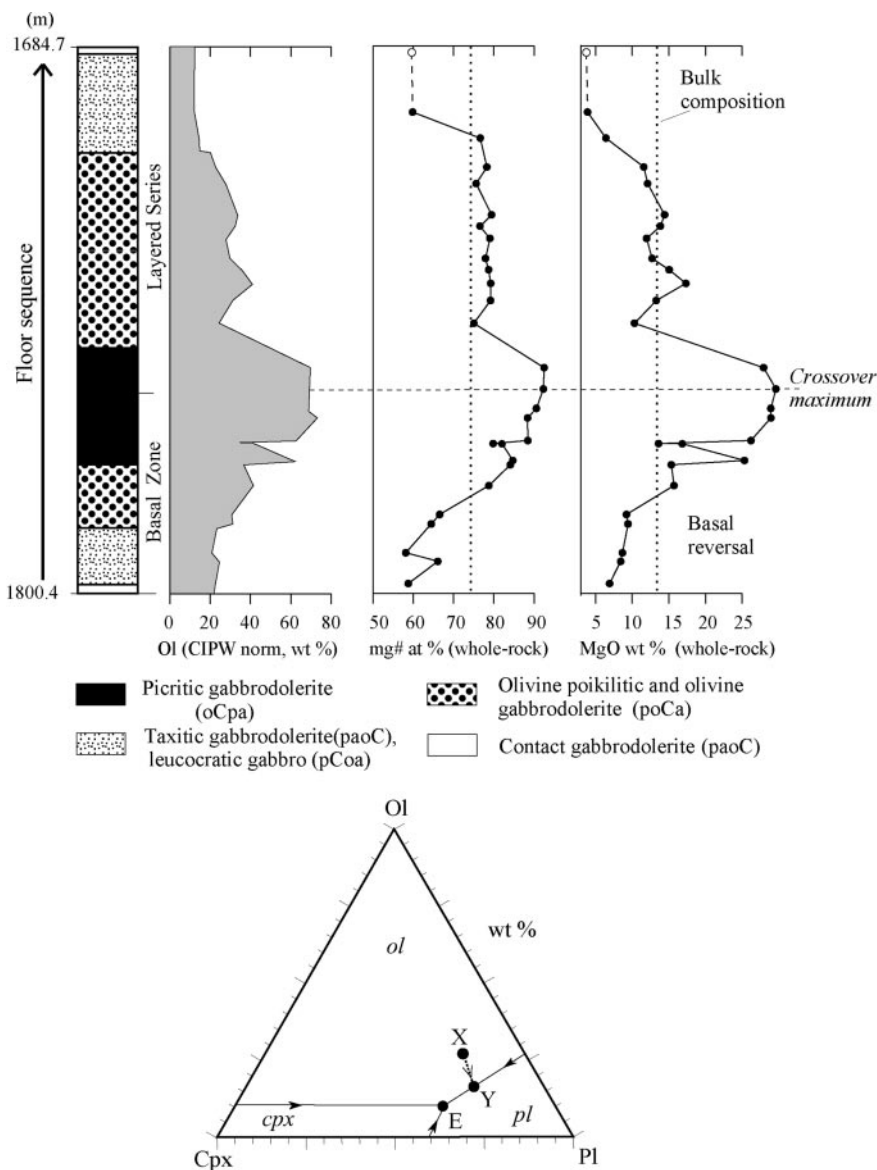


Fig. 2. Generalized stratigraphic section through the Kharayelakh sill (Noril'sk region, Russia) showing variations in % CIPW normative olivine, whole-rock mg-number and MgO wt % with height. The data are from Czamanske *et al.* (1994). The floor sequence of the sill comprises the Basal Zone and the Layered Series. The line of demarcation between the units comprising the floor sequence runs through the crossover maxima exhibiting the most primitive rock composition in the entire section of the sill. The Basal Zone of the sill exhibits a well-developed compositional reversal characterized by: (i) an inverse order of phase crystallization $Ol + Pl + Cpx \rightarrow Ol + Pl \rightarrow Ol$; (ii) a strong difference in mg-number and lack in mass balance in MgO between the lower part of the Basal Zone and the bulk composition of the intrusion; (iii) a basal mg-number enrichment trend. The name 'gabbrodolerite' is retained as it is firmly entrenched in the literature on Noril'sk. The usage was established because subvolcanic intrusions contain rocks that are too coarse grained to be properly called dolerites. Detailed clarification of this term has been given by Czamanske *et al.* (1995). A phase diagram $Ol-Pl-Cpx$ displays the trend of the initial parental magma composition X [$Ol + L (X-Y) \rightarrow Ol + Pl + L (Y-E) \rightarrow Ol + Pl + Cpx + L (E)$] consistent with the cumulus phase sequence in the overlying Layered Series. E, $Ol + Pl + Cpx = L$; mg-number = $100Mg/(Mg + Fe^{2+} + Fe^{3+})$. Phase diagram from Dubrovskii (1998).

Inverse order of phase crystallization

Perhaps the most important feature of marginal reversals that is particularly clearly developed in layered intrusions is the presence of mineral crystallization sequences, which are essentially the opposite of those in the Layered Series. For example, Stillwater,

$Opx + Pl + Cpx \rightarrow Opx + Pl \rightarrow Opx \rightarrow Ol$ (Page, 1979; Raedeke, 1982); Tsipringa, Russia, $Ol + Pl + Cpx + Pig \rightarrow Ol + Pl + Cpx \rightarrow Ol + Pl$ (Semenov *et al.*, 1995); Koillismaa, Finland, $Opx + Pl \rightarrow Opx \rightarrow Opx + Ol \rightarrow Ol$ (Alapieti, 1982); Jimberlana, $Opx + Pl + Cpx \rightarrow Opx + Pl (?) \rightarrow Opx \rightarrow Ol$ (McClay & Campbell, 1976;

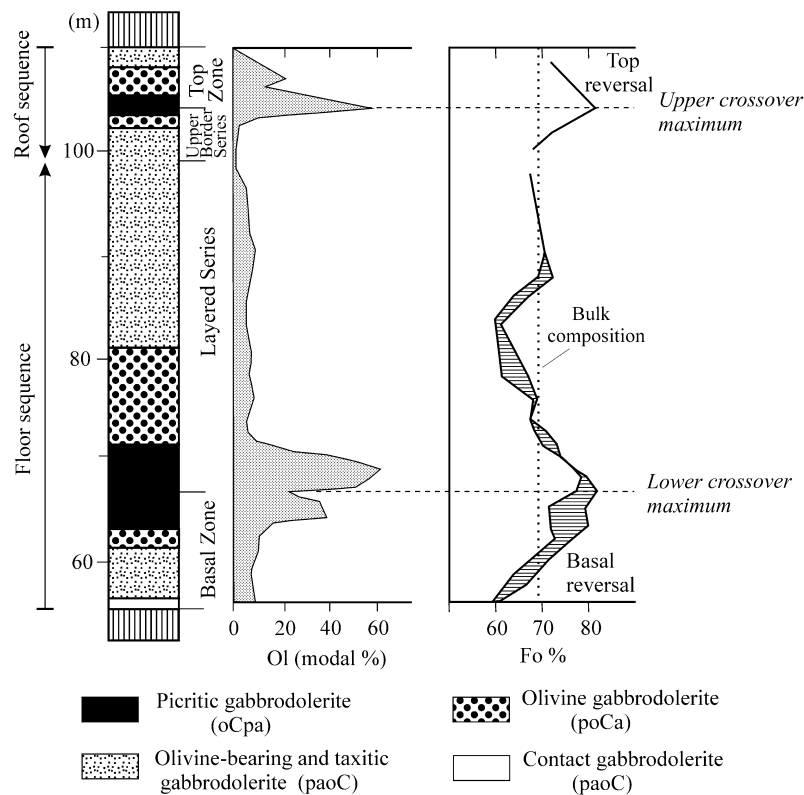


Fig. 3. Generalized stratigraphic section through the Noril'sk-I sill (Noril'sk region, Russia) showing variations in the modal % of olivine and in olivine Fo % with height. Simplified from Turovtsev *et al.* (2000). The sill is subdivided into floor and roof sequences. The floor sequence of the sill comprises the Basal Zone and the Layered Series, whereas the roof sequence contains the Top Zone and Upper Border Series. The lines of demarcation between the coupled units of the floor and roof sequences run through the lower and upper crossover maxima exhibiting the highest Fo content of olivine. The Basal Zone of the sill exhibits a well-developed compositional reversal characterized by: (i) an inverse order of phase crystallization $Ol + Pl + Cpx \rightarrow Ol + Pl \rightarrow Ol$; (ii) a difference in Fo between the lower part of the Basal Zone and the bulk composition of the intrusion; (iii) an upward Fo enrichment trend. A special feature of the sill is the double-humped shape of the compositional profile with two peaks in the concentration of modal olivine and its Fo content. The trend of crystallization of the parental magma ($Ol + L \rightarrow Ol + Pl + L \rightarrow Ol + Pl + Cpx + L$) is identical to that of the Kharayelakh sill (Fig. 2). The horizontally hatched area shows the observed range in Fo content of olivine.

Campbell, 1978); Burakovskiy, Russia, $Opx + Cpx + Pl \rightarrow Opx + Cpx \rightarrow Cpx + Ol \rightarrow Ol$ (Snyder *et al.*, 1995; Higgins *et al.*, 1997); Kivakka, Russia, $Pl + Opx \rightarrow Opx \rightarrow Opx + Ol \rightarrow Ol$ (Alapieti *et al.*, 2000) (see Table 1 for abbreviations). The Basal Zone of the Monchegorsk intrusion (Fig. 1) also exhibits a compositional reversal, which is characterized by an inverse order of phase crystallization $Pl + Opx \rightarrow Opx \rightarrow Opx + Ol \rightarrow Ol$ (Sharkov, 1980). Similar phase reversals are present at the base of sills described by Simkin (1967), but in general these are rarely documented, because of commonly small thicknesses and the fine-grained nature of the basal rocks. As an illustration, one can deduce an inverse order of phase crystallization $Ol + Pl + Cpx \rightarrow Ol + Pl \rightarrow Ol$ for the basal zones of the Kharayelakh and Noril'sk-I sills (Figs 2 and 3). An important feature is that the chilled margins are often compositionally close to the products of crystallization of the lowest melting eutectic or cotectic composition of the parental liquid

line of descent. For example, the contact gabbrodolerite of the ore-bearing sills of the Noril'sk region (Czamanske *et al.*, 1995) has a modal mineralogy and chemical composition similar to the most evolved olivine gabbrodolerite (an $Ol + Pl + Cpx + L$ eutectic point). Likewise, the chilled norite of the Monchegorsk layered intrusion is modally and chemically similar to norite at the top of the intrusion (an $Ol + Pl$ cotectic line).

Inverse cryptic layering

The inverse order of phase crystallization in marginal reversals is always accompanied by change in mineral chemistry towards more primitive compositions (e.g. more Fo-rich olivine) in moving away from a contact with the country rock. For instance, in the Stillwater Complex the lowermost interval, up to ~500 m, exhibits an upward mg-number enrichment trend.

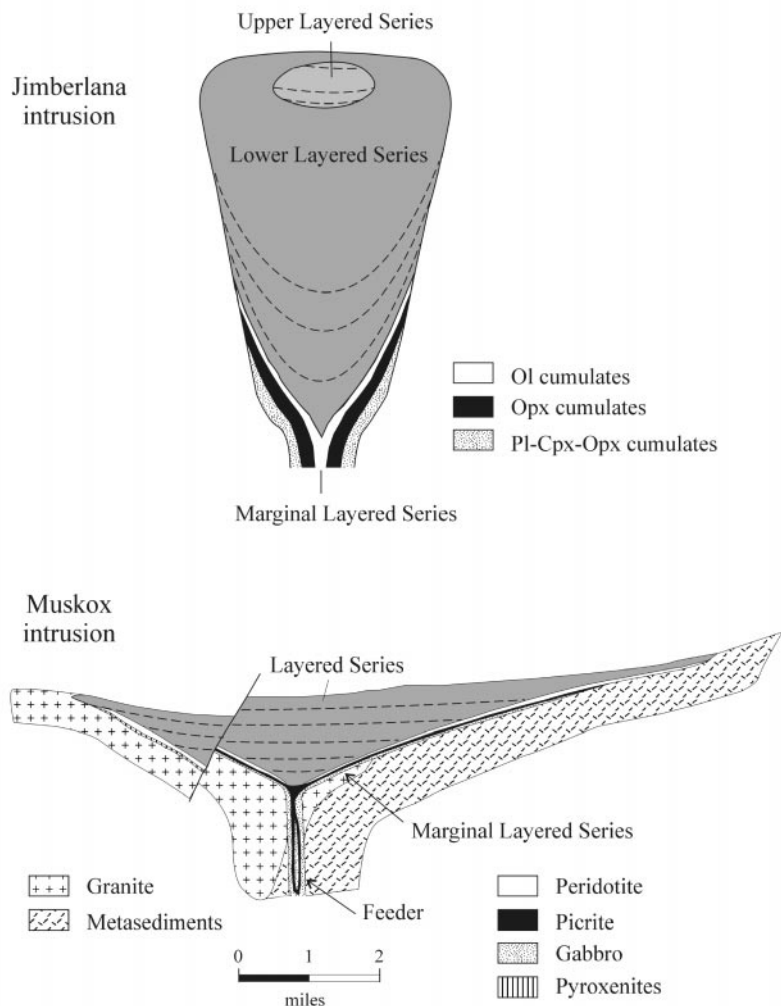


Fig. 4. Generalized sections across Jimberlana (Campbell, 1978) and Muskox (Irvine & Smith, 1967) layered intrusions showing compositional reversals developed along steeply inclined chamber margins and subvertical feeder dykes.

The mg-number of cumulus orthopyroxene increases from 76 to 86 in this interval (Raedeke & McCallum, 1984). The Muskox intrusion also has a marginal zone (120–200 m thick), which shows upward mg-number enrichment in olivine from Fo 70 to Fo 85, followed by a thick sequence of layered ultramafic rocks where olivine is in the range Fo 80–90 (Irvine, 1980). The Fongen–Hyllingen complex has marginal diorite at the base (40–220 m thick) with highly evolved mineral compositions and exhibits a systematic upward mg-number enrichment trend with mg-number in clinopyroxene increasing from 22 to 57 (Wilson & Engell-Sørensen, 1986). The Basal Zones of the Monchegorsk layered intrusion (Fig. 1) and the Kharayelakh (Fig. 2) and Noril'sk-I sills (Fig. 3) also show pronounced upward mg-number enrichment trends. It is important to note that the whole-rock and mineral compositional

trends in Figs 1–3 are not limited to the relatively evolved basal rocks but extend into the lower part of most primitive single-phase cumulate layers up to a maximum value of the mg-number. Above this the normal tendency for mg-number to decrease upwards takes over. The compositional maxima are clearly defined in some thin sills. For instance, an mg-number maximum in mafic minerals (e.g. Fo % in olivine) approximately in the middle part of picritic gabbro-dolerite units is one of the most important features of cryptic layering in the Noril'sk type intrusions (Distler *et al.*, 1979; Genkin *et al.*, 1981; Fig. 3). In thick layered intrusions, such as the Monchegorsk intrusion (Fig. 1), compositional maxima are usually less evident because of the presence of a large thickness of ultramafic rocks with very limited compositional variations. The level of such an mg-number maximum can be defined as

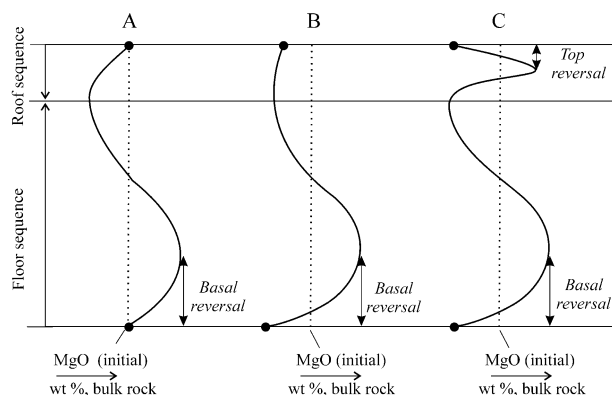


Fig. 5. Three types of vertical compositional profiles involving a refractory component (MgO wt %, bulk composition). Most models of magma differentiation (Gray & Crain, 1969; Fujii, 1974; Frenkel' *et al.*, 1988; Marsh, 1988; Tait & Jaupart, 1996, etc.) are based on profiles such as A, which is characterized by identical contents of a refractory component (e.g. MgO) in the initial parental magma and in the lower and upper chilled margins denoted by filled circles. Profiles B and C exhibit fairly well-developed basal and both basal and top reversals, respectively, which are more compatible with natural observations (e.g. Figs 1–3). The marked difference should be noted between the composition of the upper and lower margins and the parental magma based on the bulk composition expressed as wt % of a refractory component such as MgO.

the upper boundary of the marginal compositional reversals.

Cotectic composition of rocks composing marginal reversals

It is important to record the modal mineralogy of rocks in layered intrusions, to distinguish rocks of cotectic origin from those enriched in either plagioclase or olivine by mechanical processes (e.g. crystal settling or flotation, Morse, 1980). Unfortunately, detailed studies of the modal composition of rocks composing marginal reversals are rather rare. Simkin (1967) presented perhaps the most extensive data on the modal composition of rocks in the marginal reversals of alkaline basaltic sills from the island of Skye, Scotland. These data show that the lowermost rock in the marginal reversals is an olivine gabbro with a modal mineralogy (Ol 5–20%, Cpx 25–30%, Pl 50–60%) that is very close to the mineral proportions expected from liquids crystallizing along an Ol–Cpx–Pl cotectic. A similar cotectic mineral assemblage (Ol 10–15%, Cpx 10–20%, Pl 60%, + recrystallized glass) is characteristic of contact gabbrodolerites in the marginal reversals of the Noril'sk intrusions (Likhachev, 1994; Czamanske *et al.*, 1995). With respect to the olivine gabbro, the rocks of broadly troctolitic composition in the marginal reversals of the Skye and Noril'sk sills are richer in olivine (~25–30%), consistent with a higher proportion of olivine in liquids crystallizing along an Ol + Pl + L

Table 1: Abbreviations used in the paper

Pl	plagioclase
Ol	olivine
Opx	orthopyroxene
Pig	pigeonite
Cpx	clinopyroxene
Aug	augite
Qtz	quartz
Fsp	potassium feldspar
Fa	fayalite
Or	orthoclase
Ab	albite
An	anorthite
Ne	nepheline
Di	diopside
o	olivine
p	plagioclase
a	clinopyroxene
b	orthopyroxene
c	chromite
C	cumulate

In cumulates (e.g. poCb), the symbols preceding C denote cumulus phases; those that follow C denote intercumulus phases.

cotectic. Pigeonite gabbro and gabbronorite, which dominate the marginal reversals of Antarctic basic sills with S-shaped profiles (Gunn, 1966), also display a roughly cotectic composition (Opx or Pig 20%, Cpx 20%, Pl 60%). Additional evidence for the cotectic composition of rocks in marginal reversals is provided by layered intrusions. Norites composing the lowermost parts of marginal reversals in some ultramafic layered intrusions either have cotectic compositions (Opx 30%, Pl 70%) as in the Kivakka intrusion (Koptev-Dvornikov *et al.*, 2001) or are slightly enriched in Opx with respect to the cotectic composition (Opx 40–50%, Pl 50–60%) as in the Monchegorsk intrusion (Dokuchaeva & Yakovlev, 1994) and the Stillwater complex (Raedke & McCallum, 1984). As a result of the complex nature of olivine–orthopyroxene crystallization with variations in the pressure and composition of natural magmas (e.g. Longhi, 1991; Dubrovskii, 1998) it is difficult to judge how close the pyroxenite and harzburgite in marginal reversals of layered intrusions are to certain cotectic or peritectic curves. Overall, the available data suggest that the formation of marginal reversals commonly occurs from liquids of near-cotectic composition. This means that mechanical processes such as crystal settling of

phenocrysts or newly formed crystals in the chamber seem to play little or no role in the formation of the marginal reversals.

Development of marginal reversals from both phenocryst-free and phenocryst-rich parental magmas

The important feature of compositional reversals is their occurrence in igneous bodies formed from both phenocryst-laden and phenocryst-free parental magmas. An unquestionable example of the former group of bodies is the Kilauea Iki lava lake, Hawaii (Helz *et al.*, 1989) formed during the 1959 eruption of lavas with abundant olivine phenocrysts (17–20 wt %, on average). The drilled lower part of the lake displays a clearly defined marginal reversal with an upward increase in whole-rock MgO from 17.5 to ~27 wt % that is thought to result almost entirely from post-eruptive gravitational redistribution of olivine phenocrysts. Many other intrusions with marginal reversals are also considered to have been produced from phenocryst-rich parental magmas but the evidence for the existence of phenocrysts in magmas is often ambiguous (Latypov, 2003).

At another extreme is the 330 m thick quartz tholeiitic Penepplain sill, Antarctica; this is well exposed and shows no sign of containing any pre-existing phenocrysts upon intrusion (Marsh, 1996). The sill has a pronounced 100 m thick marginal reversal with a progressive upward increase in MgO from ~4 to 7 wt %. This interval also shows a steady upward increase in normative An content from 61 to 67 (Gunn, 1962). In addition, there is a clear lack of mass balance between the chilled margin (4 wt % MgO) and the bulk composition (~6 wt % MgO) of the Penepplain sill. Another example is the 85 m thick Kuz'minskii basic sill, Siberia; this has been shown to have formed from phenocryst-free magma and reveals a marginal reversal with 8 wt % MgO in the chilled margin and ~11 wt % MgO in its upper part (Frenkel' *et al.*, 1988). These observations, taken in conjunction with the cotectic composition of the rocks, strongly indicate that the presence of phenocrysts in parental magmas plays no decisive role in the formation of marginal reversals.

Development of marginal reversals along the floor, walls and roof of magma chambers

Available data suggest that marginal reversals can develop along the subhorizontal floor, steeply inclined walls and even the roof of magma chambers. Most commonly they occur at the subhorizontal floor, as is the case with many sills. Among them, for instance, are the Antarctic tholeiitic sills described by Gunn (1966).

The development of compositional reversals along inclined to subvertical chamber margins is documented for some large layered intrusions and their feeder dykes (Fig. 4). Among the most spectacular examples of marginal reversals developed along inclined walls are the Jimberlana (Campbell, 1978), Muskox (Irvine & Smith, 1967), Fongen–Hyllingen (Wilson & Engell-Sørensen, 1986), Great Dyke (Wilson, 1982), and Koillismaa (Alapieti, 1982) intrusions. In particular, in the V-shaped undeformed Jimberlana layered intrusion (Campbell, 1978) the well-developed reverse fractionation sequence occurs in layers with primary dips in excess of 80°. Moreover, in the Jimberlana and Muskox intrusions marginal reversals on inclined walls are shown to have gradational transitions into subvertical feeder dykes (Fig. 4). This is especially evident in the Jimberlana intrusion, in which the two inward-dipping marginal successions of Pl–Cpx–Opx, Opx and Ol cumulates finally converge with the formation of a vertically zoned feeder-like dyke. The feeder dyke of the Muskox intrusion is also vertically zoned, with norite forming the margins and picrite the central part. Olivine increases in grain size, abundance, and Mg/Fe ratio from the dyke margin toward the centre whereas plagioclase decreases in abundance but increases in grain size and anorthite content. In this respect the mirror parts of the dyke are reminiscent of those of the marginal reversals along the inclined walls of the Muskox intrusion. These reversals typically grade inward from bronzite gabbro at the contact through picrite and feldspathic peridotite to peridotite. The gradation is essentially marked by an increase in the concentration of olivine and is accompanied by an increase in the Mg/Fe ratio of the mafic silicates (Irvine & Smith, 1967). Thus, in some respect, the vertically zoned feeder dyke of the Muskox intrusion can also be considered as being composed of two inward-dipping marginal reversals that converge at the centre of a feeder dyke.

To my knowledge, top compositional reversals have never been reported in large layered igneous intrusions but they can be identified in some sills exhibiting olivine-rich units at their roof. As an illustration, the top reversals can be distinguished in many Siberian picrite–gabbrodolerite sills (e.g. Ryabov, 1992; Turovtsev *et al.*, 2000; Fig. 3) and in some alkaline picrite sills (e.g. Drever & Johnston, 1967; Gibb & Henderson, 1996). Top reversals seem to be a much rarer phenomenon in nature than basal or wall reversals (Fig. 5c) but must be explained by any model of magma differentiation. Overall, it is obvious that such different spatial occurrences of marginal reversals strongly suggest that the process responsible for the origin of these reversals in layered intrusions is not practically affected by gravity.

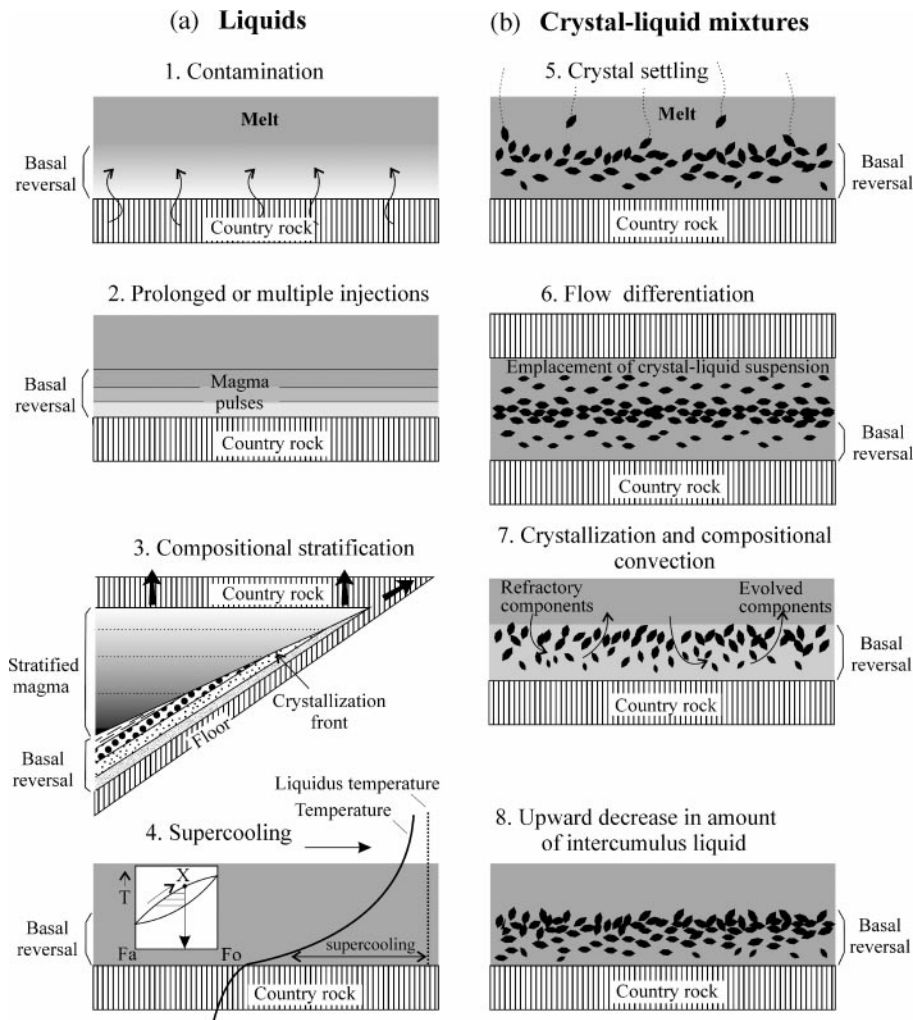


Fig. 6. Current models for the formation of marginal compositional reversals subdivided into two groups. The first group of hypotheses (a) appeals to crystallization of liquids of different composition produced by wall-rock contamination, multiple injections and compositional stratification. The second group of hypotheses (b) invokes crystallization of crystal-liquid mixtures of different composition produced by crystal settling, flow differentiation, compositional convection and an upward decrease in amount of intercumulus liquid. Also shown is a supercooling model (4) that is difficult to assign to either group. The figure showing the compositional stratification model (3) is slightly modified from Wilson & Engell-Sørensen (1986). (See text for further discussion.)

REVIEW OF CURRENT MODELS FOR THE FORMATION OF MARGINAL COMPOSITIONAL REVERSALS

Existing models for the origin of marginal reversals in igneous complexes can be rather arbitrarily subdivided into two groups, which are schematically depicted in Fig. 6. The first group of hypotheses (a) appeals to the crystallization of liquids of different composition produced by contamination, multiple injections and compositional stratification. The second group of hypotheses (b) invokes crystallization of crystal-liquid mixtures of different composition produced by crystal settling, flow differentiation, compositional

convection and an upward decrease in amount of intercumulus liquid. Also, a supercooling model is shown in Fig. 6, which is difficult to place into either of the above groups. The validity of each model for the explanation of the origin of marginal reversals is discussed in detail below.

Contamination of magma in the chamber

The first idea that comes to mind for producing highly evolved liquids at the chamber margins is certainly a change of magma composition induced by wall-rock contamination. This idea is strongly supported by the common occurrence of partially melted fragments of

country rock in the Marginal Series of many layered intrusions. Wilson & Engell-Sørensen (1986) rejected this idea, however, because it is difficult to envisage how such a mechanism could produce systematic compositional regressions. Additionally, there are a number of sills, such as the Noril'sk intrusions (Czamanske *et al.*, 1994, 1995) and the Shiant Isles Main Sill (Foland *et al.*, 2000), which show well-developed basal reversals (e.g. Figs 2 and 3), but lack appreciable signs of crustal contamination, even in terms of isotopic composition. That wall-rock contamination is not responsible for the formation of marginal reversals is also clear from the fact that the mineral sequences within the marginal reversals do not commonly change in response to a dramatic change in the composition of the adjacent country rock. For instance, in the Muskox intrusion (Fig. 4) the marginal reversal preserves the same crystallization sequence despite variations in country rock composition from metasediments to granite. Another strong argument against the contamination model is provided by the Penikat layered intrusion, Finland (Alapieti & Lahtinen, 2002), which is made up of five thick megacyclic units each showing a well-developed basal reversal despite the fact that only the lowest unit is in contact with country rock. It can also be demonstrated that contamination of magma by country rocks can produce crystallization sequences in the marginal reversals that do not necessarily duplicate those in the Layered Series.

Prolonged or multiple injections into the magma chamber

Another common explanation for the origin of marginal reversals involves variations in the composition of the magma during the continuous and prolonged filling of the chamber. The filling period of medium-sized bodies such as the Palisades Sill may vary in the range of 1–10 years (Gorring & Naslund, 1995), whereas that of large layered intrusions may occur over tens of thousands of years (Cawthorn & Walraven, 1998). Reasons for the changes of magma composition during filling vary—increasing degrees of partial melting of the mantle source, injections from stratified crustal magma chambers, the removal of varying amounts of Mg-rich minerals during magma ascent in a feeder conduit, etc. Such a mechanism has been discussed but dismissed by Wilson & Engell-Sørensen (1986). They correctly pointed out that only the first magma batches emplaced into a gradually expanding magma chamber could be envisaged as being evolved as a result of the above-mentioned processes and could contribute to formation of marginal reversals. However, marginal reversals appear to occur all along the flanks of large layered intrusions, and not only adjacent to the crystalline products of the initial magma fluxes

(e.g. Stillwater, Page, 1979; Muskox, Irvine & Smith, 1967; Fongen-Hyllingen, Wilson & Engell-Sørensen, 1986). Also, the chemical and petrographic characteristics of the chilled margins are commonly constant along the entire length of sills, suggesting either rapid, single pulse emplacement of magma (e.g. Hess, 1956) or prolonged continuous magma influxes of similar (e.g. Gorring & Naslund, 1995) or different composition, which had enough time to thoroughly mix before the onset of crystallization in the chamber.

Perhaps the strongest argument against the multiple magma injection model is that well-developed marginal reversals occur in many komatiite (e.g. Bédard, 1987) and ferropicrite (e.g. Hanski, 1992) lava flows, which have clearly crystallized from a single pulse of magma. Also, observations on protracted lava eruptions show that magma composition, as well as volume and degree of contamination, commonly can vary over fairly short periods; the duration of periods between magma successive eruptions can also vary significantly (e.g. Hawaiian lava lakes, Helz *et al.*, 1989, and references therein). Therefore it seems reasonable to expect that if marginal reversals were formed by multiple injections of magma they would exhibit compositional breaks, strong volume disproportion between rocks composing the marginal reversals, crosscutting relations and chilled contacts between the different rock types, etc. Such observations are not, however, common within marginal reversals. Thus, the possibility of large variations in the chemical composition of successive magma pulses is difficult to reconcile with the systematic compositional changes common within the marginal reversals. Taken together these observations suggest that the answer to the problem of the marginal reversals must be found in the context of a model involving a single magma pulse, either rapid or prolonged, and that the process responsible for their formation must be internally, not externally driven. It is, however, possible that changes in magma composition during chamber filling could, in some cases, make minor contributions to the final compositional structure of marginal reversals.

Compositional stratification of magma in the chamber

Wilson & Engell-Sørensen (1986) suggested that the origin of marginal reversals is consistent with crystallization during gradual elevation of compositionally stratified magma along an inclined surface in response to the influx of dense, primitive magma entering the bottom of the chamber. During enlargement of the chamber, increasingly primitive magma comes into contact with the sloping floor just below the roof and an inverted sequence of crystalline products derived from the stratified magma develops. The model

adequately explains the marginal reversal in the Fongen–Hyllingen intrusion but fails, however, to account for the occurrence of compositional reversals at the base of thin sills, which lack evidence of compositionally stratified magma and repeated or continuous magma influx, as well as crystallization along inwardly inclined margins.

Double-diffusive convection that has been proposed as the cause of compositional stratification in magma chambers has not proved as fruitful as might originally have been thought (Jaupart & Tait, 1995). McBirney (1985) and Morse (1986) first pointed out that in a crystallizing magma temperature and composition cannot vary independently because they are constrained by the liquidus relations. In all the experiments on double-diffusive convection, the liquids were superheated, and layering occurred as a result of the thermal buoyancy. This is unlikely in a system constrained to lie close to its liquidus (Jaupart & Tait, 1995).

Disequilibrium crystallization owing to high degree of supercooling

Wager & Brown (1968, p. 517) suggested that the inward increase in the Fo contents of olivine and the increase in olivine relative to orthopyroxene in dykes and marginal zones could be due to a gradual decrease inwards in the degree of supercooling. This idea can be illustrated using the T – X phase diagram Fo–Fa (Fig. 6). The main drawback of the model is that under a high degree of supercooling the composition of the chilled margin must be identical to the parental magma composition. This is not, however, the case with many basic sills and layered intrusions, which display S-shaped profiles B and C rather than A (Fig. 5). McClay & Campbell (1976) also noted that the idea of supercooling could not be applied to the Jemberlana marginal series because the high degree of supercooling required would make the marginal series a chilled margin. It is not, however, fine grained. Only a very narrow zone of chilled gabbro at the margin of this series can be formed in this way, but not the entire series. The variety of the cumulate textures and layering displayed by the Jemberlana marginal series is also difficult to reconcile with extreme supercooling. The same is true with many other layered intrusions showing well-developed marginal reversals that consist of medium- to coarse-grained rocks.

Crystal settling of phenocrysts or newly grown crystals in the chamber

Basal accumulation of phenocrysts (Gray & Crain, 1969; Fujii, 1974; Marsh, 1989) or newly grown crystals (Frenkel' *et al.*, 1988; Woster *et al.*, 1990, 1993) is

perhaps the most popular mechanism for explanation of marginal reversals in komatiite lava flows (e.g. Bédard, 1987), lava lakes (e.g. Moore & Evans, 1967; Heltz *et al.*, 1989), sills (e.g. Frenkel' *et al.*, 1988) and intrusions (e.g. Lightfoot & Naldrett, 1984). The model suggests that an upward increase in modal olivine content in marginal reversals is a consequence of a decreasing solidification rate with time that ensures a progressive increase in the amount of olivine phenocrysts able to settle to the bottom of the magma body. Important constraints on this model have been put forward by Gibb & Henderson (1992, p. 540): 'For a sill emplaced into relatively cold country rock, chilled margins will form rapidly before any of the suspended olivine crystals can sink out of the upper chill or into the lower chill. While the exact thickness of such chilled margins will depend on several factors, their existence places two often-overlooked, bounding conditions on models involving gravitational redistribution of the phenocrysts: firstly, the upper and lower chilled margins must contain the same amount of olivine; and secondly, the average olivine content of the sill must equal this amount.' In other words, compositional profiles of sills formed from phenocryst-laden magma must be consistent with profile A in Fig. 5. Principally I believe that phenocryst settling can be regarded as a possible mechanism for the formation of marginal reversals in some phenocryst-laden lava flows and lakes, which exhibit S-shaped compositional profiles close to A in Fig. 5. One good example is the Kilauea Iki lava lake (Helz *et al.*, 1989; Marsh, 1996). However, numerous data on sills and layered intrusions, summarized above, show that in the majority of cases the compositions of the chilled margins are generally much more evolved than that of the bulk intrusion. In other words, their compositional profiles are more consistent with variants B and C in Fig. 5. It is therefore clear that such a variant of the crystal settling model does not provide an adequate answer to the problem of most marginal reversals.

Gibb & Henderson (1992) envisaged only one circumstance in the crystal settling model in which chilled margins might prove to be more evolved than the bulk composition of the sill. This is where suspended olivine crystals are partially or completely removed from the marginal parts of the initially homogeneous magma by flow differentiation during emplacement of the sill (Bhattacharji, 1967; Simkin, 1967; Komar, 1972). Alternatively, the chilled margin may be a derivative liquid produced after emplacement and expelled from the centre of the magma body towards the margin. Subsequent chilling of the margins would result in olivine contents below the average of the sill. It should be emphasized that the chilled margin in these conditions is a liquid that was in chemical equilibrium with

olivine phenocrysts. Such a variant of a crystal settling model involving expelling the liquid fraction from a phenocryst-laden magma deserves more detailed consideration. To do this we focus our attention on those basic-ultrabasic layered intrusions in which marginal reversals are most well developed.

The bottom parts of the marginal reversals in many opx-rich layered intrusions, such as Stillwater, Koillismaa, Jimberlana, Burakovsky and Kivakka, are commonly composed of norite or gabbro-norite, which are much more evolved than the bulk composition of these intrusions. Let us consider the typical marginal reversal of the Monchegorsk intrusion showing the sequence $Pl + Opx$ (norite) $\rightarrow Opx$ (bronzitite) $\rightarrow Opx + Ol$ (harzburgite) $\rightarrow Ol$ (dunite) (Fig. 1). Because norite forms from magma more evolved than the bulk composition, it can be interpreted as the product of crystallization of a liquid fraction that was somehow expelled from the phenocryst-laden magma toward the chamber margins. This imposes a very strict constraint on any crystal settling model—the existence of a liquid fraction of phenocryst-laden magma that was of noritic composition. It is commonly assumed in crystal settling models that the intruding magma carries olivine phenocrysts only. Rough calculations indicate that to cover the gap between the bulk composition of the Monchegorsk intrusion (28 wt % MgO) and its chilled norite (13.4 wt % MgO) it is necessary for the intruding magma to contain >40% olivine phenocrysts. All the compositions that can be produced from a mixture of noritic liquid (Pl 50%, Opx 50) with olivine phenocrysts must lie on a line connecting the composition of the chilled norite with the olivine apex in Fig. 1b. With an increase in olivine content in olivine-liquid mixtures, orthopyroxene and plagioclase contents must progressively decrease with retention of the Pl/Opx ratio 1:1. Thus the rocks formed from such olivine-liquid mixtures will define a sequence from olivine-free norite through olivine norite and olivine-rich norite to dunite. This is clearly at odds with the observed rock sequence in the marginal reversal of the Monchegorsk intrusion, which includes, as essential elements, bronzitite (bC) and opx-rich harzburgite (boC).

Strictly speaking, our assumption above about olivine phenocrysts in equilibrium with noritic liquid is incorrect because olivine fractionation at low pressure (Fig. 1b) does not permit the production of such a noritic liquid from a parental magma X. One way to derive a noritic liquid is through differentiation of the parental magma X along a cotectic line $Ol + Opx + L$ at a pressure of $\sim 3\text{--}4$ kbar during the ascent of the magma towards the surface (Fig. 1c). High-pressure derivation of noritic liquid implies that it must be in equilibrium with both olivine and orthopyroxene. Besides, the amount of orthopyroxene must be about

twice that of olivine as follows from an intersection of an extension of the X-chilled norite line with a conode $Ol\text{--}Opx$. Rough calculations for this case indicate that to cover a gap between the bulk composition and the chilled norite the magma must carry >60% phenocrysts (20% Ol ; 40% Opx). This raises the first question. Can a magma with such a high level of crystallinity be emplaced into the present crustal location? According to Marsh (1996), a magma containing 60% phenocrysts is above the level of critical crystallinity, which is at $\sim 50\text{--}55\%$. The portion of magma in the chamber above this level is referred to as a rigid crust that is already drillable and in some respects is the effective wall rock of the magma chamber (Marsh, 1996). Let us admit that such magma can none the less be intruded. This raises a second question. Phenocrysts of olivine and orthopyroxene have approximately the same density (3.3 g/cm^3) and most probably are of the same size. Consequently their rate of settling must be similar. How can a subordinate amount of olivine in such an extremely viscous magma be separated from orthopyroxene to produce a dunite zone surrounded on both sides by harzburgite and bronzitite? Definitely this task is impracticable for gravitational forces.

The foregoing strongly suggests that a crystal settling model cannot be the process responsible for the origin of marginal reversals in sills and layered intrusions. Even the most advanced variant of this model involving chilling of the liquid fraction of the phenocryst-laden magma at the chamber margins fails to reproduce the mirror image of the marginal reversals from liquid-crystal mixtures of different composition. I have demonstrated this by the example of the Monchegorsk layered intrusion. The same is true for all other opx-rich layered intrusions with well-developed marginal reversals. In addition, it should be kept in mind that a crystal settling model is solely based on gravity and it cannot therefore explain such an important feature of compositional reversals as their capability to develop along steeply inclined margins and even on the roof of magma chambers (Fig. 4).

Flow differentiation during intrusion of phenocryst-laden magma

Bhattacharji & Smith (1964) and Bhattacharji (1967) have shown experimentally that magma flowing along a feeder can concentrate early-formed olivine phenocrysts at the centre of the dyke (the Bagnold effect). On the basis of these results, they attributed the reverse fractionation in the Muskox intrusion to successive pulses of magma precipitating high-temperature phases, which are pushed to the centre by flow. Simkin (1967) extended this idea to the sill

situation and attributed reverse fractionation in the Skye alkaline basic sills to hydrodynamic migration of particles away from margins during flow. Campbell (1978), however, correctly reasoned that grain dispersive forces produced by the Bagnold effect are small and could not produce the grain-to-grain contacts required for cumulate textures. He also noted that although flow differentiation is a valid mechanism in narrow dykes, <100 m wide (Barriere, 1976), it cannot be a factor in the development of large intrusions such as Jimberlana and Muskox. An important objection to the flow differentiation mechanism was raised by Wager & Brown (1968, p. 517). They drew attention to the fact that the olivines in the Muskox feeder range in composition from F_{085} to F_{060} . This represents a large range in temperature of crystallization and, if equilibrium was maintained between the magma and olivines of composition F_{060} in the feeder and the layered series, the feeder must have remained open while 1.6 km of layered rocks were deposited. This objection is also true of Jimberlana intrusion (McClay & Campbell, 1976). Flow differentiation has been also found inadequate for explanation of the reverse modal grading observed within komatiite lava flows (Bédard, 1987).

Crystallization and compositional convection in a thermal boundary layer

Jaupart & Tait (1995) and Tait & Jaupart (1996) proposed that during the evolution of magma in a chamber, compositional convection allows for the continuous exchange between melt in the pores of the cumulus pile within the thermal boundary layer and the main magma reservoir. In this process the dense refractory components are delivered from the main magma body into the cumulus pile while light evolved components flow in the opposite direction. The model suggests that very close to the lower contact of the intrusion the phenocryst-free magma is chilled to a solid before compositional convection in the thermal boundary layer can have any impact and consequently the composition of the chilled margin will be equal to the initial magma composition. Moving up from the lower contact, one passes regions where compositional convection has caused significant chemical exchange with the overlying reservoir—leading to the formation of rocks that are richer in refractory components (e.g. MgO) than the initial magma. The resulting compositional profile produced within this framework of crystallization + compositional convection is consistent with profile A in Fig. 5. The principal disadvantage of the model is that the composition of the chilled margins is close to the parental magma composition in this case. This is not, however, the case with many

basic sills and layered intrusions, which exhibit the profiles B and C rather than A (Fig. 5). In addition, similar to a crystal settling model, it can be shown that the simple addition of an increasing amount of a refractory component, such as MgO, to the initial magma composition cannot produce an order of phase crystallization that is the opposite of that observed in the Layered Series.

Upward decrease in amount of intercumulus liquid

Raedeke & McCallum (1984) attributed the basal mg-number enrichment reversal in the Stillwater complex to the reaction of cumulus orthopyroxene with decreasing amount of trapped intercumulus liquid. They suggested that the amount of trapped liquid is highest in the lowermost rocks because heat loss to the floor causes strong cooling and rapid accumulation of orthopyroxene and trapped liquid during the initial stage of crystallization. The reaction of the intercumulus liquid with the coexisting orthopyroxene produces iron-rich pyroxenes. Higher up in the section, the amount of trapped liquid in the cumulate rocks decreases because more of the intercumulus liquid can be squeezed back into the main magma chamber owing to compaction and other processes. As a result, the high ratio of cumulus orthopyroxene to trapped liquid results in only minor readjustment of the pyroxene composition, which therefore remains more magnesium rich. This model can explain only one feature of marginal reversals, namely, mineral compositional trends that are the inverse of those in the Layered Series. However, the model provides no explanation for the most important feature of marginal reversals—their mirror images as reflected by reverse phase crystallization sequences.

SUMMARY OF MOST IMPORTANT CONSTRAINTS ON THE REQUIRED MECHANISM FOR MARGINAL REVERSAL FORMATION

It is clear from the preceding discussion that none of the current models can provide an adequate explanation for the mirror image (with respect to the Layered Series) of the marginal compositional reversals observed in many sills and layered intrusions. Their origin still remains uncertain. It is instructive to summarize briefly some important constraints following from the above analysis and pertinent to any model for the origin of marginal reversals.

(1) It is clear that the evolved composition of chilled margins, mineral crystallization sequences and trends of mineral composition, which are essentially the opposite of those in the Layered Series, represent common features of sills and layered intrusions and are not anomalous features. Such marginal reversals are developed in igneous bodies regardless of their size and bulk composition. This strongly suggests that the Layered Series and their mirrors—marginal reversals—in each specific intrusion are produced from the same parental magma (Wilson & Engell-Sørensen, 1986). Therefore any attempts to explain the universal features of marginal reversals by appealing to some external and unpredictable processes such as multiple magma emplacements will be ineffectual. This conclusion is also strongly supported by the occurrence of clearly defined marginal reversals in many lava flows, which have crystallized as closed systems. Obviously the answer to the problem of the marginal reversals must be found in the context of a model of a single magma pulse.

(2) It is significant that marginal reversals are composed of rocks with a roughly cotectic composition. This suggests that they formed without any significant contribution from settling phenocrysts. This means that the magmas parental to mafic-ultramafic plutonic bodies generally contained only small amount of phenocrysts, which could not therefore have any significant impact on the formation of marginal reversals. This is strongly supported by the occurrence of clearly defined marginal reversals in several igneous bodies thought to have formed from phenocryst-free parental magmas. Thus the desired mechanism must be capable of producing marginal reversals from phenocryst-free or phenocryst-poor parental magmas.

(3) The reverse mineral crystallization sequences and cotectic composition of rocks in marginal reversals strongly indicates their successive formation from magma compositions spanning, in reverse sequence, the liquid line of descent of the parental magmas. Whatever process is responsible for the formation of marginal reversals, it must be able to produce a range of liquid compositions from an initially homogeneous parental magma.

(4) The ability of compositional reversals to develop equally well along both subhorizontal and subvertical margins and even roofs of magma chambers significantly shortens the list of mechanisms that can be potentially responsible for their origin. In particular, such a popular mechanism as gravitational crystal-liquid differentiation can be safely excluded from this

list. The required mechanism must be practically independent of gravitational forces.

(5) The thermodynamic conditions of marginal rock crystallization are characterized by the occurrence of a significant temperature gradient that is imposed by cold country rock on hot magma at the chamber margins, particularly during its juvenile stage of evolution. It therefore seems reasonable to suggest that it is the temperature gradient that is a driving force of the process responsible for the formation of compositional reversals.

To sum up, the process required to explain the origin of marginal reversals must be capable of producing a range of liquid spanning in reverse sequence the liquid line of descent of parental phenocryst-poor magma at the floor, walls and roof of magma chambers. The question that remains to be answered is what is the nature of this universal physicochemical process that causes liquid-state separation ranging from the lowest temperature eutectic points through all intermediate lines and surfaces to an initial composition in the volume of one phase? One can safely reason that the only known process that is not dependent on gravity forces is diffusion. The only type of diffusion that can provide substantial chemical separation of initially homogeneous silicate liquids in a temperature gradient at the magma chamber margins is thermal or Soret diffusion. This mechanism of magma differentiation is, however, currently out of favour amongst most petrologists for a number of reasons. Therefore, before applying Soret fractionation to explain the origin of marginal compositional reversals we have to analyse why this mechanism was dismissed as an important process in petrogenesis (Leshner & Walker, 1991).

PHYSICAL AND CHEMICAL ASPECTS OF Soret FRACTIONATION IN EXPERIMENTS AND NATURE

A short history of application of Soret fractionation in igneous petrology

The Soret effect was predicted (Ludwig, 1856) and experimentally demonstrated (Soret, 1879) more than a century ago. The Soret effect arises from the internal redistribution of species within a substance in response to an imposed temperature gradient. Diffusion of species up and down thermal gradients results in chemical differentiation of an originally homogeneous liquid. Attempts to apply the Soret effect to igneous petrology have a long history excellently outlined in a number of publications (e.g. Spera *et al.*, 1982; Walker & Delong,

1982; Hess, 1989; Leshner & Walker, 1991; Wilson, 1993).

One can distinguish at least two main time periods when Soret fractionation fell in and out of fashion as a mechanism for magma differentiation. It is curious that the reasons for its falling into disfavour were distinctly different on the two occasions. It was initially rejected on physical grounds whereas on the second occasion it failed for chemical reasons. Soret fractionation originally became popular among petrologists at the end of the 19th century (Lagorio, 1887; Brögger, 1890) in response to Soret's (1879) spectacular experiments carried out in aqueous solutions. The formation of mafic border zones in specific zoned plutonic bodies was attributed to the operation of Soret diffusion in a thermal gradient between cool country rocks and the hot interior of the chamber. At the beginning of the 20th century, however, the Soret hypothesis fell into disfavour mainly because of strong criticism by Bowen (1921, 1928). Bowen (1928) concluded that diffusion cannot be important in magmatic processes because heat conduction (10^{-2} – 10^{-3} cm²/s) is orders of magnitude faster than chemical diffusion (10^{-5} – 10^{-9} cm²/s), so a magma would freeze long before diffusion could accomplish much fractionation. He also argued that the Soret effect would have no importance in natural igneous differentiation because the magnitude of the effect was predicted to be very small.

A second phase of interest in silicate liquid thermal diffusion among petrologists arose in the late 1970s and early 1980s, and stemmed chiefly from Hildreth's (1977, 1979, 1981) suggestion that Soret fractionation may play an important role in some subvolcanic silicic magma chambers. Largely in response to this suggestion, experiments were undertaken to characterize the Soret effect in silicate liquids (Walker *et al.*, 1981; Leshner *et al.*, 1982; Walker & Delong, 1982). These clearly established that Bowen's physical arguments for dismissing the importance of the Soret effect in magmatic differentiation were actually wrong (Schott, 1983). First, these studies demonstrated that naturally occurring silicate melts exhibit dramatic thermal diffusion effects, which are fully comparable in magnitude to crystal fractionation in producing chemical separation within a temperature gradient. Second, it was recognized that arguments involving the relative magnitudes of heat and chemical diffusivity are valid only in a static environment, but not in a dynamic one. The key to accomplishing Soret fractionation is to keep the diffusion length short. This was resolved by combining Soret diffusion with thermal convection (Shaw *et al.*, 1976; Hildreth, 1977, 1979, 1981; Spera, 1977). This model suggests that, within a convecting magma body,

thermal differences will not be distributed uniformly but rather will be compressed into thin regions along the solidifying margins. The development of such narrow thermal boundary layers substantially reduces the diffusion length scale over which the Soret effect must operate. It was also stressed that convection can actually enhance Soret separation by removing fractionates and renewing nutrients to the diffusion zone (Wahl, 1946; Shaw *et al.*, 1976; Hildreth, 1981; Spera *et al.*, 1982; Schott, 1983). In other words, the convecting magma acts as a feeding system that continually brings fresh magma to the boundary layer, thereby limiting the diffusion to the mass transport across the narrow contact between the boundary layer and convecting magma body. The physical reasons for Soret fractionation being insignificant for magmatic differentiation were consequently eliminated.

It is ironic, however, that while resolving the physical impediments, the Soret diffusion experiments introduced a new, much more serious, obstacle for the application of this mechanism to magmatic systems. It emerged that the chemical fractionation produced by the Soret effect in silicate liquids does not resemble that seen in either mafic or felsic igneous rock suites (Walker & Delong, 1982; Leshner, 1986; Leshner & Walker, 1986). Leshner & Walker (1991) made a direct comparison between natural observations and experimental data and found that there is little agreement between these two datasets. In particular, the most abundant oxide, SiO₂, is enriched in the low-temperature, early eruptive unit of the Bishop Tuff, whereas it is the principal constituent of the hot Soret fraction in laboratory experiments. Leshner & Walker (1991) concluded from this comparison that the Soret effect was not an important agent in the differentiation of the Bishop Tuff, contrary to the earlier proposition of Hildreth (1981), and found no evidence for its large-scale operation in other rhyolitic systems (Ludington, 1981; Whalen, 1983). Their conclusion that thermal diffusion is not an important agent for magmatic differentiation remains widely accepted (Leshner & Walker, 1991). Therefore, any model invoking Soret diffusion as a mechanism for magmatic differentiation must first find an adequate explanation for the lack of convergence between chemical fractionation in nature and Soret diffusion in the laboratory. If such explanation can be found, it provides an opportunity to revive the hypothesis of Soret fractionation.

Comparison of *P*–*T* conditions in natural magmatic systems and experiments on Soret fractionation

The basic magmas that crystallize to form sills and layered intrusions have traditionally been considered

to be relatively 'dry', mainly because of the paucity of hydrous minerals. Fluid-saturated conditions are considered to be significant only during the latest stages of magmatic differentiation. Recently this notion has been challenged (Boudreau, 1992, 2002; Boudreau *et al.*, 1997). Boudreau (2002) presented several lines of evidence, including the high Cl/F ratio and Cl and H isotopic signature of halogen-bearing minerals, suggesting that the Stillwater, Bushveld and other high-Cl layered intrusions crystallized from magmas that contained in excess of 1 wt % H₂O. He also stressed that although volatile components can have a marked effect on the crystallization behaviour of the magmas parental to the layered intrusions, most existing models for the crystallization of these intrusions either ignore or downplay their significance. Boudreau's idea is strongly supported by phase equilibria analysis of the mechanism of magma intrusion that was originally carried out by Fyfe (1970) and further developed by Dubrovskii (1984, 1993, 1998). Latypov (2002) has suggested that actually all types of magmas parental to plutonic bodies must have been wet and crystallized under fluid pressure. This conclusion clearly follows from the topology of anhydrous and water-saturated solidus–liquidus curves in natural granitic, basaltic and alkaline systems. As an example, Fig. 7 shows the topology of the solidus–liquidus curves of basalt in *P–T* space. Only completely dry basalt such as X¹ (Fig. 7b) can reach the Earth's surface and erupt as lava at temperature Z well above its 1 atm liquidus without volatile exsolution during its ascent. All water-bearing basalts such as a melt X² (Fig. 7c) with 2 wt % H₂O will rise and begin to lose water near Y, where they cross a corresponding vesiculation isopleth and will start to crystallize on a liquidus line at Z, being water saturated. If the densities of the host rocks and the magma at Z are similar, the magma will cease to rise and start to form a plutonic body. It is widely accepted that dissolved volatiles, dominated generally by H₂O, are present in nearly all terrestrial magmas (Johnson *et al.*, 1994). Therefore all types of water-bearing magmas giving rise to plutonic bodies must inevitably intersect the corresponding vesiculation isopleth on their way towards the Earth's surface. As a result, these magmas will exsolve water as a separate phase at this point and begin to crystallize as water-saturated melts when reaching their liquidus. There can be envisaged only one possibility for magma to escape water-saturated conditions at the onset of crystallization. The rising superheated magma must be arrested physically at considerable depth, say, at point K (Fig. 7c) and then slowly cooled to a point M on the liquidus, where it starts to crystallize, being water bearing but not water saturated. But even in this case magma will soon become water saturated as a

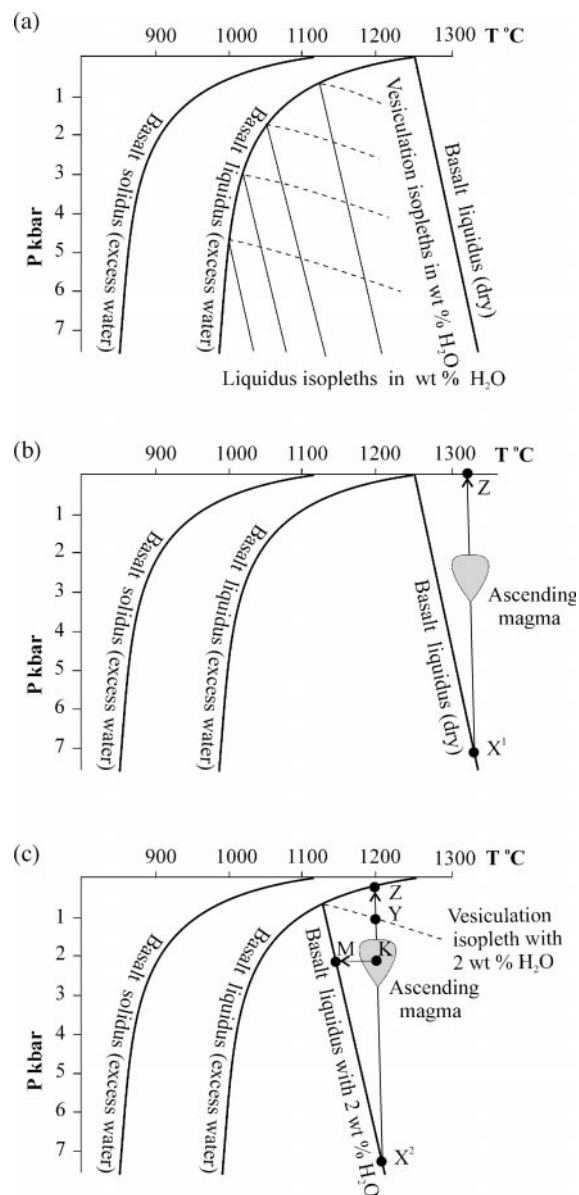


Fig. 7. (a) Anhydrous (dry) and water-saturated liquidus and solidus equilibria for basalt [modified from Condliffe (1976); solubilities used in the construction of water-saturated lines are from Hamilton (1964) and Holloway & Blank (1994)]. The liquidus isopleths, labelled with wt % H₂O contents in the melt, are the *P–T* coordinates where solid phases crystallize from a melt containing dissolved H₂O. The vesiculation isopleths, labelled with wt % H₂O contents in the melt, mark the *P–T* coordinates of gas bubble exsolution in the system on release of pressure. (b) and (c) show schematic representation of the ascent of dry and water-bearing magma towards the Earth's surface, based mainly on Fyfe (1970) and Dubrovskii (1993, 1998). (See text for further explanation.)

result of progressive crystallization of anhydrous phases. Plutonic bodies formed from such magmas are relatively rare because of the very substantial erosion needed to bring them close to the Earth's surface.

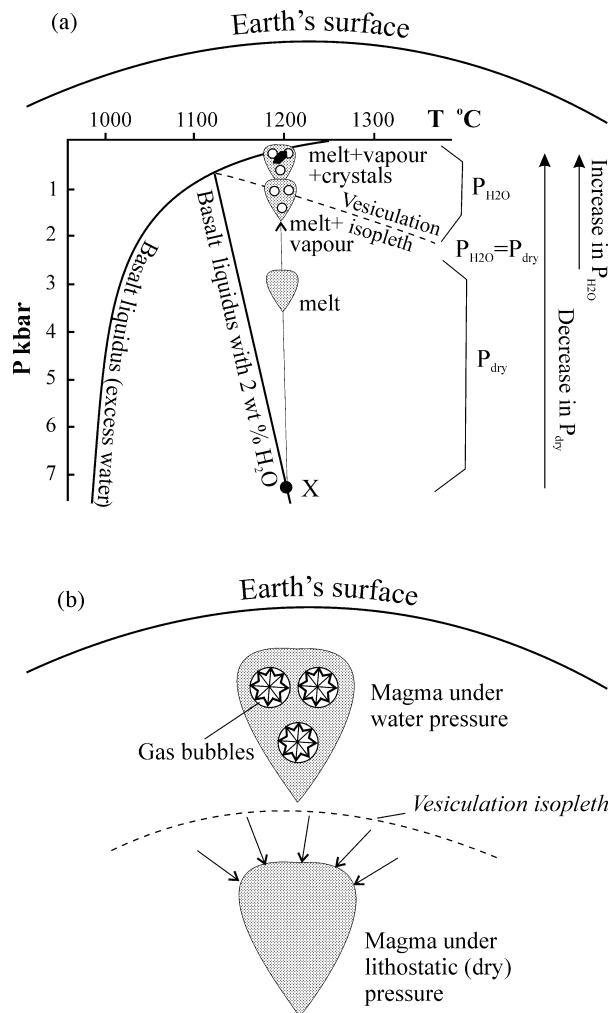


Fig. 8. (a) Schematic depiction of the relationship between lithostatic pressure (dry pressure or P_{dry}) and water pressure ($P_{\text{H}_2\text{O}}$) showing that magma during its ascent towards the Earth's surface and subsequent crystallization in crustal magma chambers can be either under lithostatic pressure when subjected to the external pressure of overlying rocks, or under fluid pressure when subjected to the internal pressure of gas bubbles after intersection of the vesiculation isopleth (b). (See text for further explanation.)

It is instructive here to clarify a point regarding the relationship between the lithostatic pressure (dry pressure or P_{dry}) and water pressure ($P_{\text{H}_2\text{O}}$) that a magma experiences during its ascent and subsequent crystallization in a crustal magma chamber (Fig. 8a). It is often overlooked that $P_{\text{H}_2\text{O}}$ can be either equal to or higher than P_{dry} but it can never be less than P_{dry} in water-saturated magmas (Dubrovskii, 1984). One cannot speak about $P_{\text{H}_2\text{O}}$ if under a given lithostatic pressure all volatiles are dissolved in the melt. For instance, basalt X (Fig. 8a) on its way from the site of magma generation to the vesiculation isopleth is under lithostatic 'dry' pressure despite containing 2 wt % of

dissolved water. Only upon reaching the vesiculation isopleth, where basalt becomes water saturated and exsolves a separate fluid phase, does $P_{\text{H}_2\text{O}}$ equal P_{dry} . An increase in the amount of the fluid phase during further magma ascent towards the Earth's surface will provide a progressive rise in the fluid pressure $P_{\text{H}_2\text{O}}$. The fluid pressure during magma ascent increases in contrast to the lithostatic pressure, which decreases. The isochoric crystallization of magma that starts upon its reaching the liquidus will result in a further increase in $P_{\text{H}_2\text{O}}$. In most, but not all, cases substantial internal overpressure is unlikely to be attained, however, because of volatile loss through the chamber walls. It seems most likely that magma in the chamber will be under water pressure equal to or slightly above the corresponding lithostatic pressure throughout the duration of crystallization. It follows from the foregoing that magma can be either under lithostatic pressure, as a consequence of the external pressure of the overlying rocks, or under fluid pressure equal to or greater than P_{dry} when subjected to the internal pressure of gas bubbles (Fig. 8b). There is no intermediate situation between these two extreme cases. Therefore the total pressure that magma experiences in the chamber cannot be composed of the sum of lithostatic and fluid pressures as is mistakenly stated in some publications.

The common objection to the idea that plutonic bodies form from fluid-saturated magmas is the preponderance of anhydrous assemblages over hydrous ones. It should be emphasized in this connection that the absence of hydrous phases such as amphibole or mica in these bodies does not actually preclude their formation from a water-saturated magma. It may simply indicate that the fluid pressure and consequently the water content of the magma was not high enough for hydrous phases to appear on the liquidus. Merzbacher & Eggler (1984) showed that up to 4–5 wt % dissolved water is necessary to stabilize hornblende in basaltic to dacitic melts. The minimum fluid pressure at which amphibole appears on the liquidus in a basaltic system is 1–1.5 kbar (Yoder & Tilley, 1962; Condcliffe, 1976; Spulber & Rutherford, 1983). The rare occurrence of cumulus amphibole in basic-ultrabasic intrusions can therefore be explained by their crystallization at a fluid pressure of < 1–1.5 kbar (Fig. 9) and corresponding water contents of ~1–2 wt % (Fig. 7a). The latter is in line with Boudreau's (2002) estimation of the water content of the parental magmas for many layered intrusions. Under such pressure the crystallization of amphibole-free olivine gabbro bodies spans the temperature interval from approximately 1150 to 950°C (Fig. 9). For basic magmas of more MgO-rich composition the temperature interval will be shifted towards somewhat higher temperatures.

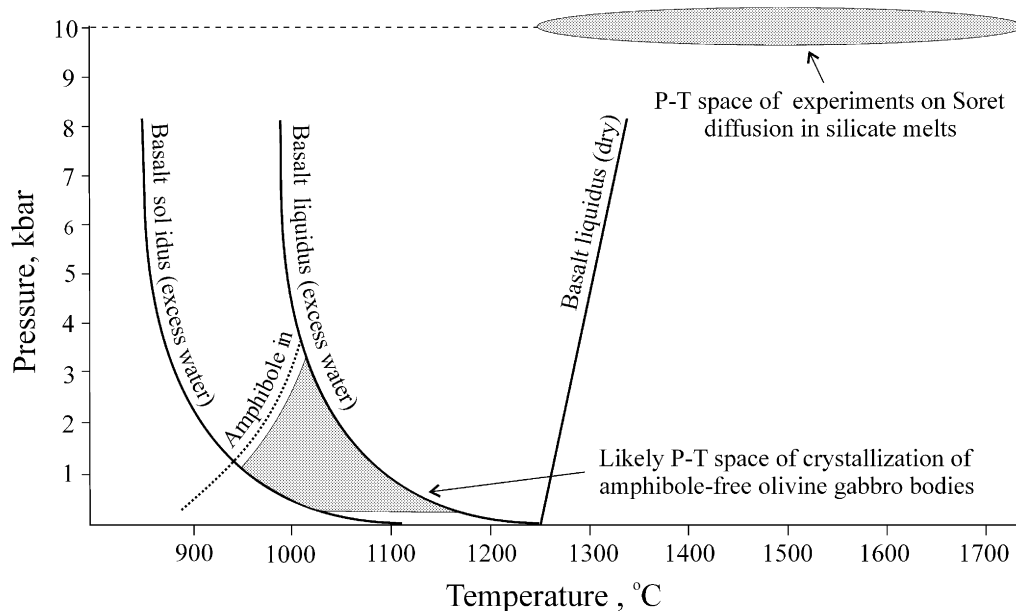


Fig. 9. Pressure–temperature diagram showing the great difference in P – T space between the crystallization of amphibole-free olivine gabbro bodies and the experimental studies on Soret diffusion in silicate melts. Liquidus–solidus equilibria are from Condcliffe (1976); the Soret diffusion field is based on the data of Walker *et al.* (1981), Leshner *et al.* (1982), Walker & Delong (1982), Leshner (1986) and Leshner & Walker (1986, 1991).

In some cases the absence of cumulus hydrous phases can be also related to the composition of the basaltic magma. Sisson & Grove (1993) have recently demonstrated that hornblende stability is very sensitive to the Na_2O content of the bulk basalt composition, with the result that hornblende can form as a near-liquidus mineral in water-saturated sodic basalts, but does not appear until liquids reach andesitic compositions in moderate Na_2O basalts. They concluded that the absence of hornblende in basalts with low-to-moderate Na_2O contents (i.e. the typical parental magma compositions of most basic layered intrusions) is not therefore evidence that those basalts are nearly dry.

To sum up, phase equilibria analysis unambiguously shows (Fig. 7c) that any ascending water-bearing basaltic magma can reach its liquidus and start to crystallize only after intersection with its vesiculation isopleth. This indicates that any basaltic magma, at the onset of its crystallization, must be already water saturated and be under water pressure. Water pressure in crystallizing crustal basaltic magma chambers does not commonly exceed 1–1.5 kbar, and therefore there are no marked records of fluid activity such as change in the sequence of mineral crystallization, appearance of hydrous phases and anorthite-rich plagioclase and wollastonite-rich clinopyroxene (Johnson *et al.*, 1994). However, dissolution of 1–2 wt % H_2O in basaltic

magma at this pressure is known to have a dramatic effect on its liquidus temperature, viscosity, transport properties, etc. Therefore any successful model for magma fractionation in crustal chambers must give special emphasis to the water-saturated state of natural magmas.

The above estimation of P – T conditions for crystallization of mafic–ultramafic plutonic bodies differs significantly from those of laboratory studies of the Soret effect in silicate liquids (Walker *et al.*, 1981; Walker & Delong, 1982; Leshner, 1986; Leshner & Walker, 1986, 1991). These studies have all been conducted on dry silicate liquids, at 10 kbar pressure and temperatures of 1500–1750°C at the hot end of a thermal gradient and 1250–1400°C at the cold end (Fig. 9). One may therefore question whether experiments conducted at 10 kbar, at temperatures exceeding the liquidus by hundreds of degrees and under anhydrous conditions will be an adequate guide to the expected behaviour of natural melts crystallizing in crustal magma chambers. Leshner & Walker (1991), however, considered that these differences do not place serious limitations upon the direct application of the laboratory data to natural systems for several reasons. First, their experimental studies of a wide variety of magma compositions failed to identify a resolvable temperature dependence in the character of Soret separations. Second, it was shown that Soret diffusion at high T

produces chemical separations indistinguishable from liquid immiscibility under isothermal conditions at considerably lower magmatic temperatures. Hence there are no indications from the available experimental data that silicate speciation significantly changes within a few hundreds of degrees of the liquidus. Walker & Delong (1982) also noted that high experimental pressures do not pose a serious threat to the relevance of the experimental results, as no large pressure influence on the Soret effect is theoretically anticipated. The validity of the above arguments seems to be beyond question. Nevertheless, in the following sections I will explore the natural situations in which the qualitative character of Soret fractionation could be substantially different from the experimental simulations.

Soret fractionation in near-liquidus water-saturated magmatic systems

The localities and time period for operation of Soret fractionation in nature

Soret fractionation in magma chambers can arise only in those localities in which extreme temperature gradients can be maintained for a relatively long time (Spera *et al.*, 1982; Leshner & Walker, 1991). A dynamic environment in which vigorous magma convection establishes a liquid thermal boundary layer adjacent to the chamber margins meets these requirements (Fig. 10). In comparison with a static environment, the exchange of heat between a convecting magma body and its surroundings is more rapid here and so the body as a whole cools more rapidly (Fig. 10, temperature profiles from 1 to 3). But this rapid cooling is accomplished by maintaining the high temperature gradients over the short distance of the thermal boundary layer. The opportunities for Soret fractionation in natural environments remain, however, only as long as a high thermal gradient persists locally. Hence, Soret fractionation must be viewed as a transient mechanism of differentiation possible only during thermally juvenile magmatic stages when the essential thermal gradients exist in liquid boundary layers (Leshner & Walker, 1991). Situations are, however, possible when the operation of Soret fractionation can be ineffective from the very beginning of magma evolution in the chamber. This can happen, for instance, if magma is emplaced into a consolidating igneous massif that is still hot or into hot country rocks previously heated by high-temperature regional metamorphism. Because of the minor cooling effect from the country rock, the magnitude of the thermal gradient in the boundary layer can prove to be inadequate to initiate Soret fractionation.

Liquid boundary layers as open systems tending to a stationary non-equilibrium state

The critical point for further discussion is that despite the magma in the chamber as a whole representing a closed system, the liquid boundary layer can be regarded to some extent as an open system (Fig. 10a). This is because it exchanges both energy and matter with the overlying main magma body and also energy with underlying country rock and then with a growing cumulus pile. It is therefore reasonable to expect that a liquid boundary layer subjected to a temperature gradient can be maintained out of equilibrium for a transient period with the tendency toward a stationary non-equilibrium state (Ortoleva, 1994). Despite the fact that Soret fractionation initiated by such a temperature gradient is a typical non-equilibrium process, a stationary state may develop in liquid boundary layers given a sustained temperature gradient and sufficient time. That is, thermal diffusion may reach a dynamic balance with the homogenizing tendency of chemical diffusion. In the following discussion it is demonstrated that liquid boundary layers in a stationary non-equilibrium state may adjust their compositions and consequently their liquidus temperatures to an externally imposed temperature gradient (Fig. 10b).

To understand why and how Soret fractionation adjusts the composition of liquid boundary layers to an imposed temperature gradient let us consider Fig. 11a. An important feature of Soret experiments is that liquid fractionation in a superheated region is not subjected to phase equilibria constraints. As a result, the character and extent of liquid fractionation in experiments are by no means related to and limited by any liquidus surfaces, lines and points that are pertinent to the given systems at subliquidus temperatures. As an example in a superheated region of the simple binary system An–Qtz the composition X can be differentiated into a full spectrum of liquids ranging from An rich at the cold end to Qtz rich at the hot end of a thermal gradient (Fig. 11a). In more complex systems the independence from phase equilibria is clearly reflected in the ability of Soret-produced liquids to freely intersect liquidus lines and thermal barriers (Leshner & Walker, 1991). In contrast, Soret fractionation in natural magmas that are rarely superheated predominantly occurs under near-liquidus conditions and, therefore, should be expected to be affected by phase equilibria constraints. It is well known (e.g. Morse, 1980), however, that if no crystals are present in the system the composition of the melt is unconstrained with respect to the liquidus. This must be true, however, only for the equilibrium processes in closed systems. A non-equilibrium process of Soret fractionation in boundary liquid layers that act as

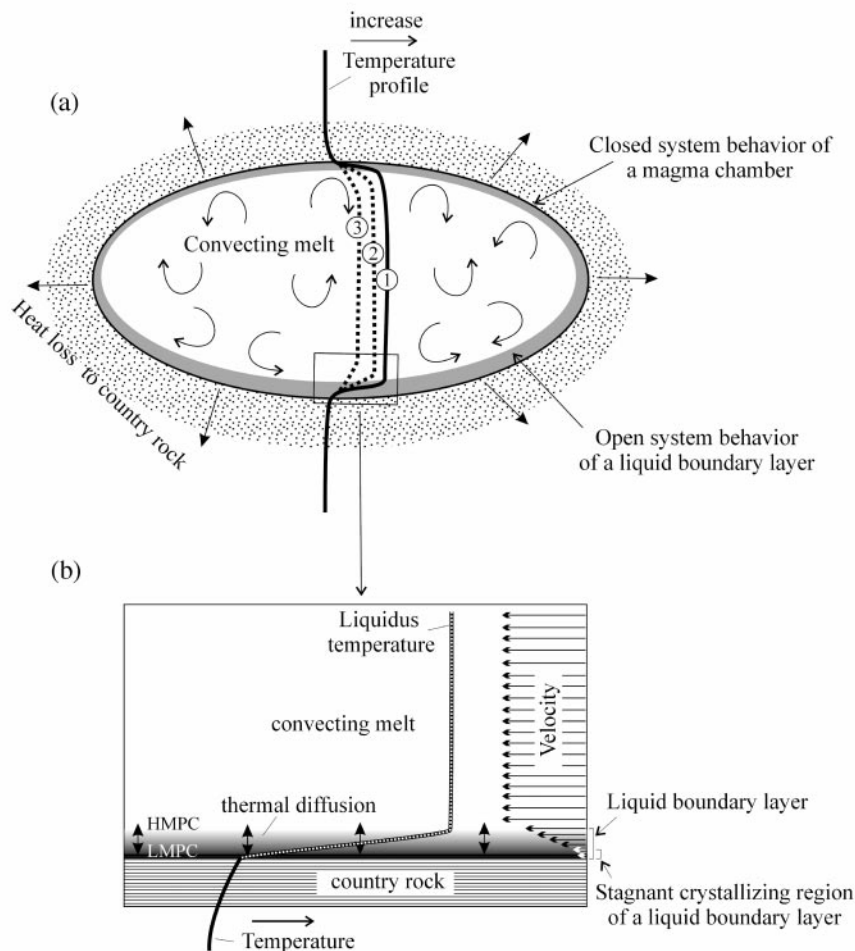


Fig. 10. (a) Schematic illustration of the decay (1, 2, 3) in the temperature gradient between a magma and its surroundings in a vigorously convecting magma chamber. The magma's velocity gradient prevents the temperature gradient from dissipating spatially by compressing it within the thin liquid boundary layer (grey shaded) at the chamber margins. Despite the magma in the chamber as a whole representing a closed system, the liquid boundary layer can be regarded as an open system exchanging both energy and matter with the overlying main magma body and also energy with the surrounding country rock and the growing cumulus pile (see also Fig. 16). It is suggested that a liquid boundary layer in which a temperature gradient is imposed is maintained out of equilibrium with the tendency toward a stationary non-equilibrium state. The latter is attained when the compositions of the melts (and their liquidus temperatures) composing the boundary layers are adjusted to an imposed temperature gradient (b). The compositional adjustment occurs by transfer of high melting point components (HMPC, e.g. An in Fig. 11a) from the liquid boundary layer into the main magma body and low melting point components (LMPC, e.g. Qtz in Fig. 11a) in the opposite direction. Mass transfer is provided by Soret-induced diffusion across the thermal boundary layer, aided by vigorous natural convection in the main magma body. The self-nucleation and crystallization of minerals occurs predominantly in the stagnant lowermost regions of the boundary layers against pre-existing crystals of the same species. (See text for further explanation.)

open systems tending to a stationary non-equilibrium state does not follow this rule.

Let us consider what can happen when the same composition X is subjected to a temperature difference $T - T^1$ within a boundary layer at the chamber margin (Fig. 11a). Let us allow that the degree of oversaturation in the liquid boundary layer is slight so that the onset of homogeneous nucleation and subsequent crystallization is sufficiently delayed. Because the liquids in a boundary layer $X - X^1$ are undercooled with respect to their liquidus they are in a metastable state. Consequently the system will tend to attain a new state of

chemical equilibrium. What can the system do in the situation when it cannot get rid of oversaturation through nucleation and crystallization? The system needs to find a way to remove the liquids from the field $An + L$. To do this it has two possibilities: either to raise the temperature of the liquids or to change their compositions. As the energy of the magma in the chamber is only enough to maintain a temperature gradient, it is only possible to change their composition. The system can do this by continuous mass exchange with the main magma body. The main agent of this mass exchange is Soret diffusion in the

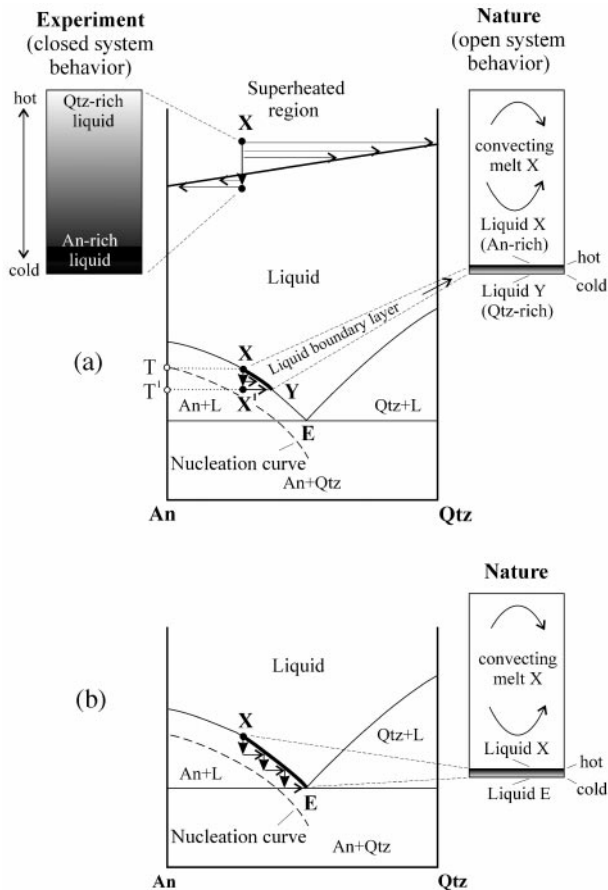


Fig. 11. (a) The phase diagram An–Qtz schematically illustrating the fundamental difference in the conditions of liquid fractionation in natural magmatic environments and Soret experiments. In a superheated region liquid fractionation is not subject to phase equilibria constraints. Therefore the character and extent of liquid fractionation are not related to, or limited by, any liquidus elements (surfaces, lines and points). A composition X exposed throughout to a temperature gradient (in the closed system of a crucible) is differentiated into the full spectrum of liquids ranging from An rich at the cold end to Qtz rich at the hot end of a thermal gradient. In contrast, liquid fractionation in near-liquidus natural magmas is governed by phase equilibria constraints. The same composition X subjected to a temperature gradient $T-T^1$ in a thin liquid boundary layer with open-system behaviour will tend to achieve a stationary non-equilibrium state on the liquidus line An + L. Given delayed nucleation and crystallization, achievement of the stationary non-equilibrium state is accomplished by transfer of an excess of the anorthite component from the boundary layer into the overlying main magma body and a simultaneous flux of the Qtz component in the opposite direction. The mass transfer is provided by thermal diffusion aided by thermal convection in the main magma body. (b) The series of such step-like changes in composition of the liquid boundary layer will finally result in a range of liquids (interval X–E) spanning, in reverse sequence, the liquid line of descent of the parental magma X. It should be noted that the range of liquids produced here is much smaller in comparison with, and is compositionally the reverse of, that observed in the superheated region. Qtz-rich liquids are concentrated at the cold end of the thermal gradient whereas An-rich liquids concentrate at the hot end. (See text for further explanation.) E, An + Qtz = L.

liquid boundary layer aided by thermal convection in the main magma body.

To move the liquids away from the field An + L, the excess An component must be removed or/and replaced by a Qtz component. In a more general sense, this means that the system must provide a flux of high melting point components (HMPC) from the boundary layer into the main magma body and low melting point components (LMPC) in the opposite direction. Obviously, mass exchange will stop operating as soon as all the liquids composing the boundary layer X–X¹ are out of the field An + L; i.e. when they reach the liquidus line An + L (the interval X–Y). This is why, even in the absence of crystals, the liquids X–X¹ will find their place on the liquidus line An + L because it represents a boundary of the field in which location of the liquids is thermodynamically forbidden. Because liquids on this line are already in a stable state, any further change in their compositions is unlikely to proceed. Thus, in conditions of delayed nucleation, the combined operation of two processes—progressive cooling and continuous mass exchange with the main magma body—will force the liquids in the boundary layer to follow continually along the liquidus line An + L. The series of such step-like changes in the composition of the liquid boundary layer (Fig. 11b) will eventually result in a range of liquids (an interval X–E) spanning in reverse sequence the liquid line of descent of the parental magma X. I define such a state with a range of liquids lying along a liquidus line and sustained in a corresponding temperature gradient as a ‘stationary non-equilibrium state of the liquid boundary layer’. It is necessary, however, to stress that it remains unclear whether the liquidus $T-X$ curve corresponds to the true $T-X$ curve for stationary state Soret diffusion or not. Theoretical studies of this problem have not been yet conducted (M. Ghiorsio, personal communication, 2002).

It should also be noted that the depletion of the liquid boundary layer in HMPC requires the corresponding enrichment of the overlying magma in HMPC to maintain mass balance. In this process the liquidus temperature of the overlying magma will gradually rise with time and that potentially can lead to its compositional oversaturation. Two principally different scenarios can be envisaged here. If the magma is slightly superheated, or on the liquidus but almost phenocryst free, the chemical impact on the magma is rapidly diluted in the main magma body via convection, and the compositional oversaturation, if it occurs, will be uniformly distributed throughout the magma in the chamber. If magma is on the liquidus with a small amount of phenocrysts the oversaturation can be readily diminished to nothing by the growth of phenocrysts suspended in the convecting magma. As a result,

the entire column of magma in the chamber will be maintained constantly close to its liquidus temperature. The latter and the former variants are considered in this and a companion paper (Latypov, 2003), respectively.

The evolution of the composition of liquid boundary layers in a stationary non-equilibrium state

It is important to realize that the first liquid boundary layer formed at the chamber margins can comprise liquid compositions spanning almost the entire liquid line of descent of the parental magma in reverse sequence. The uppermost liquid in this boundary layer will always be consistent with the parental magma's composition, whereas the lowermost liquid, depending on the temperature of the country rock, can occupy any position along a liquid line of descent of the parental magma. It is the temperature of the country rock that solely determines the composition of the lowermost liquid in the first boundary layer. This temperature can be lower or higher than that of the lowest melting point of the liquid line of descent of the parental magma. In the former case, which seems most probable for natural environments, the composition of the lowermost liquid in a boundary layer will be adjusted to this lowest melting point. In the latter case, the lowermost liquid will lie somewhere on the liquidus path from the lowest melting point to the initial magma composition. Upon progressive decrease in magnitude of the thermal gradient related to the growing, insulating cumulus pile, and an overall fall in the temperature of the whole magma body, the compositional characteristics of the liquid boundary layer in the stationary state will tend to become more and more primitive. It is not difficult to foresee that in this process the composition of the lowermost liquid in the boundary layers will progressively cover the entire liquid line of descent of the parental magma. It is important to bear in mind, however, that the compositional adjustment will only work perfectly given favourable kinetic conditions for the operation of Soret fractionation. Unfavourable kinetic conditions can greatly limit or even preclude the adjustment of the liquid compositions in the boundary layer to an imposed temperature gradient.

The recording of compositional variations in liquid boundary layers in stationary states into the solid rocks

The compositional variations within liquid boundary layers in stationary states are the result of maintaining a temperature gradient. These variations will, therefore, disappear without leaving a trace upon dissipation of the temperature gradient with cooling if they

are not locked into the solid rocks. Hence the developing stationary states must be accompanied by concurrent crystallization that progressively records the developing compositional variations in the boundary layers into the solid rocks. The pertinent question here is how does crystallization occur in liquid boundary layers? Most probably nucleation and crystallization occur only in the stagnant lowermost regions of the boundary layers (Fig. 10b). This is because the activation energy for homogeneous nucleation is much higher than that for heterogeneous nucleation, and consequently the amount of supercooling required for homogeneous nucleation is appreciably greater than that for heterogeneous nucleation (Campbell, 1978, 1996). The amount of supercooling in a crystallizing magma chamber that loses heat by conduction through its wall rocks is estimated to vary from 1° to 20°C (Martin *et al.*, 1987; Martin, 1990). The degree of supercooling required to produce homogeneous nucleation in a basaltic magma is not known but is unlikely to be less than those for pure metals, which vary between 77°C for mercury and 319°C for nickel (Campbell, 1996). Therefore, despite the fact that magma throughout the chamber, including the liquid boundary layer, is close to its liquidus, crystallization will occur essentially as overgrowths on pre-existing crystals of the same species at the floor, walls and roof of the intrusion.

There is another question concerning the mechanism of recording the compositional characteristics of liquid boundary layers into solid rocks. The point is that, despite the fact that Soret diffusion is a process not affected by gravitational forces, the stability of Soret-produced liquids in boundary layers is gravity dependent. If liquid boundary layers are not gravitationally stable, they will be continuously destroyed as they form, as a result of convection. Liquid density varies as a function of both temperature and composition. The fall of temperature always increases melt density. The impact of changes in melt composition with differentiation on its density is more difficult to predict. The fractionation of high proportions of plagioclase will tend to increase melt density (Morse, 1986) whereas a contemporaneous increase in the SiO₂ and volatile contents will, on the contrary, result in a decrease of the melt density (Jaupart & Tait, 1995). The common occurrence of marginal reversals at the floor of sills and layered intrusions suggests that in most circumstances the combined effect of temperature and composition is in favour of gravitational stability of the floor boundary layers. The predominant stability of the floor liquid boundary layer was advocated by Carrigan & Cygan (1986). The rare existence of top reversals suggests that in some cases an upper liquid boundary layer could be also long lived or stable. Its stability can probably be

provided by the high concentration of volatiles in the upper part of intrusions, which causes a significant decrease in the melt density of roof liquids (Cardoso & Woods, 1999).

It should be emphasized, however, that existence of marginal reversals along subvertical walls, where liquids in no circumstances can be gravitationally stable, strongly indicates that there is no actual need for the entire liquid boundary layer to be gravitationally stable for a record to be left in the resultant rocks. A situation can be envisaged when dynamic equilibrium between continuous growth of a liquid boundary layer and its destruction by convection is achieved, with only a thin, perhaps several millimetres thick, stagnant or slightly mobile region against the margins not being involved in large-scale convection. The stagnant region of the boundary layer adjacent to the front of crystallization or crystal accumulation can be the part of the liquid that will be most immediately incorporated into the cumulates during their consolidation (Walker & Delong, 1982). Thus the overall growth of floor, wall and roof cumulates can proceed essentially at the expense of this stagnant region of liquid boundary layers.

Some quantitative aspects of Soret fractionation in natural environments

Discussion of the quantitative aspects of Soret fractionation in natural systems is a hard task because of many uncertainties in the estimation of the controlling parameters. The range of reported values for some parameters is exceptionally wide. For instance, the rate of a Soret steady-state development in a 1 m thick liquid boundary layer, depending on the magnitude of a diffusion coefficient involved, could vary from 30 years (Schott, 1983) to 50 000 years (F. J. Spera, personal communication, 2002). The average accumulation or growth rate of the cumulus pile in convectively cooling large intrusions is reported to range between 1 cm/year (Morse, 1979, 1986) and hundreds of metres per year (Brandeis & Jaupart, 1987). The lifetime of the liquid boundary layers is estimated to range from hundreds of years (Carrigan & Cygan, 1986) to a few years (Huppert & Sparks, 1980). Natural convection in plutonic bodies is argued to be highly vigorous (e.g. Huppert & Sparks, 1980; Martin *et al.*, 1987; Jaupart & Tait, 1995) or nonexistent (Marsh, 1988, 1989, 1990; Gibb & Henderson, 1992; Mangan & Marsh, 1992). It is difficult to escape the impression that application of such a wide range of boundary conditions in calculations can reduce any numerical models to nothing more than a pure mathematical exercise, which may produce almost any results one desires. One can demonstrate, for instance,

that the magma in the chamber is predominantly in turbulent motion (Sparks, 1990; Huppert & Turner, 1991) or nearly stagnant (Marsh, 1990, 1991) simply by adopting in modelling a very high or very low Rayleigh number, respectively. One must therefore keep in mind that any estimation based on the results of numerical models will inevitably suffer from the assumptions lying at their hearts. With this in mind, a simple estimation is presented below, which is intended to demonstrate that Soret fractionation has a promising potential to be effective in basaltic magmas during the juvenile stage of their differentiation. To what extent this estimation is reliable chiefly depends on the reliability of data taken from the corresponding numerical models.

Typical marginal reversals are commonly 10–100 m thick. At first sight this is decidedly not a diffusion length scale and therefore represents a problem for any putative mechanism based on mass transport by diffusion. For even large diffusion coefficients, say 10^{-6} cm²/s, the characteristic diffusion distance is considered to be on the scale of metres in a million years (Hess, 1989). Clearly, under such conditions, the melt in the chamber will completely solidify before any liquid fractionation by thermal diffusion is accomplished. It is therefore not surprising that thermal diffusion was initially dismissed as a principal agent of igneous differentiation by Bowen (1921, 1928). However, as discussed above, this argument is compelling only in a static environment when the diffusion length is considered to be of the same order as the size of the magma body. The idea about magma chamber evolution through thin thermal boundary layers resolves the problem. The development of such narrow thermal boundary layers substantially reduces the diffusion length scale over which the Soret effect must operate. The thickness of natural thermal boundary layers is suggested to be of the order of a few centimetres, with an initial thermal gradient across them of $>100^{\circ}\text{C}$ (Walker & Delong, 1982).

Let us now to compare the rate of development of Soret fractionation in such liquid boundary layers with the known accumulation or growth rate at the margins of igneous bodies. To estimate the rate at which Soret steady state is achieved in liquid boundary layers within mafic–ultramafic magma bodies it is necessary to have a reliable set of data on chemical diffusivity of species measured in (1) basaltic melts under (2) fluid-saturated conditions, with $P_{\text{H}_2\text{O}} < 1\text{--}1.5$ kbar, and with (3) no or little initial contrast in major element composition, especially SiO₂. The second requirement follows from the conclusion reached previously about the fluid-saturated state of nearly all parental magmas to layered plutonic bodies. The third constraint is dictated by the recent finding that chemical diffusion

between couples of strongly contrasting matrices (e.g. basalt and rhyolite) can be orders of magnitude slower than in a homogeneous matrix (van der Laan *et al.*, 1994). The use of diffusivities determined based on diffusion couples of contrasting composition may not be appropriate for Soret effects that start to operate in natural basaltic melts with no chemical gradients and reach steady state with only a relatively small gradient in SiO₂ concentration. There are surprisingly few experimental studies of chemical diffusion in basaltic compositions and none of them completely satisfy the above criteria. The only experiment at low water pressure (Yoder, 1973) is not relevant to our case because of the use of a basalt–rhyolite couple with a very high difference in SiO₂ content (24 wt %). Several experiments on chemical (Medford, 1973; Dowty & Berkebile, 1982; Zidarov *et al.*, 2001) and tracer diffusion (Hofmann & Magaritz, 1977; Magaritz & Hofmann, 1978) were performed in basaltic melts with little or no initial chemical gradient in SiO₂ concentration at atmospheric pressure. All these studies show diffusivities for major and trace elements in the range of 10⁻⁶–10⁻⁷ cm²/s at 1200–1300°C. These results basically reinforce Bowen's (1921) classical determination of diffusivity (10⁻⁶–10⁻⁷ cm²/s at 1500°C) between a molten diopside and plagioclase couple that was also characterized by little SiO₂ contrast.

The main drawback of the above experiments is, however, the fact that they were all carried out using anhydrous basaltic melts. Diffusion rates in magmas are extremely sensitive to the H₂O content of the magma, so that models of rate-controlled processes in hydrous magmas may be grossly in error if 1 atm diffusivity values are used (Watson, 1981). Unfortunately, data for chemical diffusion in hydrous basaltic melts at low fluid pressure and with a low SiO₂ gradient are currently lacking. It was shown, however, by Koyaguchi (1989) that chemical diffusion of SiO₂ in an H₂O-saturated basalt–dacite couple at 1200°C and 10 kbar is two orders of magnitude faster than in dry runs for the same bulk composition and *P*–*T* conditions. There are also numerous data summarized by Watson (1994) demonstrating that the effect of H₂O on both tracer and chemical diffusion, mostly in dacitic and granitic melts, is always positive and very large, sometimes amounting to several orders of magnitude at a given temperature. On these grounds one can reasonably predict an increase of about two orders of magnitude in the chemical diffusivity of major and trace elements in H₂O-saturated basaltic melts in comparison with that in anhydrous basalts at 1 atm. This will result in chemical diffusivities in H₂O-saturated basaltic melts at low water pressure in the range of 10⁻⁴–10⁻⁵ cm²/s at 1200–1300°C. The estimate is valid for nearly all magma components, even those at only

parts-per-million concentration, because their diffusivities in multicomponent melts are shown to be similar to, and appear to be controlled by, the diffusivity of the principal melt structure-controlling species, SiO₂ and Al₂O₃ (Watson & Baker, 1991). Alkalis (Na, K, and Rb) appear to diffuse much more rapidly, however, both in hydrous and anhydrous melts. For instance, alkali diffusivities in an anhydrous dacite–rhyolite couple at 1 atm were estimated to be five orders of magnitude above the diffusivities measured for other non-alkali elements (Baker, 1990). In basaltic melts the difference between the diffusivities of alkali and non-alkali cations is likely to be less dramatic, but still significant probably, not less than 1–2 orders of magnitude. This gives chemical diffusion of alkali cations in H₂O-saturated basaltic melts in the range of 10⁻²–10⁻⁴ cm²/s. Consistent with this estimation is the suggestion by Chekhmir *et al.* (1985) of a value of 10⁻² cm²/s for *D*_{H₂} in molten water-saturated basalt, which is comparable with the diffusion of heat.

The rate of development of the Soret effect in a liquid boundary layer under static conditions can be calculated from the following equation:

$$\Delta c_i / c_i (1 - c_i) = S_T \Delta T (1 - e^{-t/\theta}) \quad (\text{Schott, 1983})$$

where $\Delta c_i = c_i(\text{cold}) - c_i(\text{hot})$, c_i is the initial mass fraction of component i , S_T is the Soret coefficient, ΔT is the temperature difference and t is time. $\theta = L^2 / \pi^2 D$ is referred to as the characteristic time for the attainment of the steady rate, where L is the thickness of a boundary liquid layer and D is the diffusion coefficient. From this equation the time for the system to reach Soret steady state (t) is given by

$$t = 3\theta = 3L^2 / \pi^2 D \quad (\text{Schott, 1983; Table 2}).$$

It is clear from Table 2 that the formation of a liquid boundary layer 2–5 cm thick with a diffusion coefficient in the range 10⁻⁴–10⁻⁵ cm²/s will require only several hours or days. This is short compared with the crystallization time for sills and layered intrusions. In reality, the time period could be even shorter because diffusion rates for melt components in fluid-saturated liquid boundary layers may be significantly accelerated relative to those in less saturated parts of the magma body. The marginal zones of large intrusions commonly show abundant evidence of high fluid activity in the form of coarse-grained and pegmatitic rocks (e.g. Kozlov, 1973), the presence of various hydrous minerals (e.g. Upton & Wadsworth, 1967), and sometimes even amygdales (Sluzhenikin, 2000). This is probably related to the preferred migration of any coexisting fluid phase towards the cold regions of thermal gradients at the chamber margins, as experimentally observed for komatiitic bulk compositions

Table 2: Effect of the thickness of the liquid boundary layer for the time necessary to reach steady state
 $t = 3\theta = 3L^2/\pi^2D$

Soret fractionation for $t = 3\theta$	L (cm)	$D = 10^{-4} \text{ cm}^2/\text{s}$	$D = 10^{-5} \text{ cm}^2/\text{s}$
$\Delta c_i/c_i(1 - c_i)$	2	3.4 h	1.4 days
$= S_T \Delta T = 1.0$	3	7.6 h	3.2 days
	4	13.5 h	5.6 days
	5	21.1 h	8.8 days

The following values are used in the calculations: $D = 10^{-4} - 10^{-5} \text{ cm}^2/\text{s}$ at $1200 - 1300^\circ\text{C}$, $S_T = 10^{-2} \text{ }^\circ\text{C}^{-1}$ and $\Delta T = 100^\circ\text{C}$ (Walker & Delong, 1982).

(Walker *et al.*, 1988). The migration of F and Cl (Leshner & Walker, 1991) and dissolved water in silicate melts (Chekhir & Epel'baum, 1990) towards the cold end of a thermal gradient is also well known from experimental studies on Soret diffusion. It is not inconceivable, therefore, that the preferred migration and accumulation of bubbles in a liquid boundary layer may result in their adhesion with the formation of a continuous network of channels penetrating the layer and acting as paths for diffusive transport of components dissolved in the fluid phase. It has been demonstrated that the diffusivities of components such as silica, iron and other divalent cations through aqueous fluids at $900 - 1300^\circ\text{C}$ are extraordinary high ($D = 10^{-2} - 10^{-4} \text{ cm}^2/\text{s}$) in comparison with most other geological mass transport coefficients and approach the diffusivity of heat (Watson, 1991; Watson & Wark, 1997). Combined mass transfer through the melt and fluid phase in a liquid boundary layer could probably result in a 'bulk' diffusivity of the order of $10^{-3} \text{ cm}^2/\text{s}$ that could provide the formation of a liquid boundary layer 2–5 cm thick in only 0.3–2.1 h. It is important to note in this context that there are factual observations suggesting that diffusion in basaltic magmas can occur at much faster rates than currently accepted. For instance, Cawthorn & McCarthy (1980) came to the unexpected conclusion that an exceptionally strong depletion in the Cr content of magnetite from the Upper Zone of the Bushveld Complex required *in situ* crystallization with the rate of diffusion in the range of 1.3×10^{-1} to $6.5 \times 10^{-4} \text{ cm}^2/\text{s}$.

An appreciation of the rate of crystal accumulation in sills and layered intrusions may be gained from the approach of Irvine (1970), who developed models for heat flow from intrusions in which solids accumulated

on the floor and convection occurred within the largely liquid interior. Using these models Morse (1979, 1986) calculated that the accumulation rate in large layered intrusions, such as the 8.4 km thick Kiglapait intrusion with 1 Myr of solidification time, was in the range of 1.3–0.4 cm/year (1 cm/year on average). Martin *et al.* (1987) estimated a rate of advance of the crystal pile in large magma chambers of the order of 10 cm/year. An average rate of accumulation of ~ 30 cm/year has been proposed for the formation of the cyclic units of the Muskox intrusion (Irvine, 1970). A rate of accumulation of ~ 1 m/year was suggested for the basal rocks of the Bushveld complex (Cawthorn & Walraven, 1998). The two latter estimates are comparable with the reported accumulation rates in relatively small sheets and sills. For instance, from the data of Gorring & Naslund (1995), the average accumulation rate in the 300 m thick Palisades Sill with 700–1000 years of solidification time is in range of 35–45 cm/year. Jaeger (1968) specifically studied the progress of solidification away from a contact for various magma conditions. In particular, he demonstrated that after 5 years of convective cooling the solidification region of the intrusion will be confined in a range of roughly 7–14 m from the contact with the country rocks. This gives an average rate of accumulation of between 1.4 and 2.8 m/year. In the frame of their convective–cumulative model, Frenkel *et al.* (1989) have estimated that a rate of accumulation of the order of 1–10 m/year will persist during the whole period of consolidation of small or medium-sized sills.

Thus, given rates of chemical diffusion in the range $10^{-3} - 10^{-4} \text{ cm}^2/\text{s}$, a Soret steady state in a 5 cm thick liquid boundary layer can be achieved in only 2–21 h. During the same time period the cumulate pile will grow by 4–7 mm at the most, given a rate of accumulation of 2–3 m/year. It follows that Soret fractionation has quite enough time to accomplish chemical separation in the thin liquid boundary layers and be therefore effective during the formation of the marginal series of layered intrusions. The formation of marginal series can be envisaged as the progressive inward movement of a 5 cm thick liquid boundary layer, the lowest, stagnant part of which is continuously consumed by the growing cumulate pile. At a rate of accumulation of 2–3 m/year, the time required to produce a marginal series 10–100 m thick, in small and medium-sized bodies, will vary from a few years to tens of years, respectively. From the onset to the end of marginal series formation the temperature contrast in the liquid boundary layer will decrease from $\sim 100^\circ\text{C}$ to nearly zero. The pertinent question here is can a sufficient thermal gradient be maintained in the liquid boundary layer during the time period of marginal zone formation? Some appreciation of this problem may be gained from the work of Huppert & Sparks (1980). They

treated, in particular, the case of an interface that forms between a 100–300 m thick hot picrite layer and a colder, overlying few kilometres thick layer of MORB magma. Both upper and lower layers convect internally with little mass transport across the interface. Huppert & Sparks calculated the thickness and life expectancy of this interface for choices of parameters appropriate for this system and found that a temperature contrast of more than 100°C to nearly zero could persist over a period of a few years across a boundary layer 1–2 cm thick. This estimation refers to the case when heat is transferred to the upper basaltic layer at a rate that greatly exceeds the heat lost to the surrounding country rock. It may be expected, therefore, that for small and medium-sized intrusive bodies, where heat loss occurs only to the surrounding rocks, especially if they are preheated during the filling of the magma chamber, the temperature contrast in the boundary layers could be maintained over tens of years or more. This is quite enough to produce 10–100 m thick marginal reversals in small and medium-sized bodies.

In large layered intrusions the time required to produce marginal reversals of the same thickness, and consequently the time for the temperature contrast to be maintained, will be longer because of the relatively slower rate of accumulation. This does not present a serious problem, however, inasmuch as large layered intrusions and even medium-sized sills are not filled instantly but rather formed by continuous influxes of magma into the chamber over a relatively long period of time. Filling of large layered intrusions may occur over tens of thousands of years (Cawthorn & Walraven, 1998). The continuous influx of hot magma may therefore supply additional energy for rejuvenation of vigorous convection and maintaining a high thermal gradient at the margins during the juvenile stage of magma differentiation in the chamber (Walker & Delong, 1982). Spera *et al.* (1982) have specifically shown that continuous recharge of magma chambers will tend to produce a steady-state thermal system with a thermal lifetime independent of the size of the chamber but instead dependent only on the mass rate of recharge. If the mafic magma intrusion rate is high enough, a steady-state or quasi steady-state convective regime can be set up and maintained for thousands of years. This conclusion can obviously be extended with little or no extrapolation to the case of a magma chamber with liquid thermal boundary layers progressively advancing inwards with time as a result of continuous growth of the cumulate pile along the chamber margins. It should be noted that the results of the theoretical analysis by Carrigan & Cygan (1986) and Cygan & Carrigan (1992) suggesting the implausibility of Soret fractionation in magma chambers will be

overturned if one takes into account the fluid-saturated state of natural magmas, which may provide considerable enhancement of chemical diffusivity and a prolongation of the residence time of horizontal liquid boundary layers.

Concluding remarks

It seems clear from the above discussion that Soret fractionation could be a powerful non-equilibrium process capable of producing a range of liquids spanning, in reverse sequence, the liquid line of descent of the parental, phenocryst-poor, magma at the chamber margins. In other words, it is exactly the process we need to explain the origin of compositional reversals in basic–ultrabasic sills and layered intrusions. The primary reason why the Soret effect has so far been ignored as an agent of differentiation is that Soret chemical fractionation in experimental silicate liquids does not resemble that seen in any igneous rock suite. In the light of the above analysis the reason for such a lack of convergence seems obvious. Unlike experimental charges, natural liquid boundary layers evolve as open systems that exchange matter with the main magma body. As a result of this, Soret fractionation in natural non-superheated liquid boundary layers is controlled by liquidus phase equilibria even in the absence of solid phases. In contrast, liquid fractionation in Soret experiments takes place in a highly superheated region independent of phase equilibria constraints. For this reason the direct correlation of experimental results with natural observations is hardly justified for this particular case. One needs, however, to say that at present the direct experimental evidence that would provide support for the proposed direction of Soret fractionation in liquidus silicate melts is missing. The available experimental data (Fig. 12) are limited to the study of thermal diffusion in superliquidus silicate melts (Walker & Delong, 1982; Leshner, 1986; Leshner & Walker, 1986, 1991) and thermal migration—a complex process working in crystal–melt mushes (Leshner & Walker, 1988; Walker *et al.*, 1988). The process of most interest for the present discussion—thermal diffusion in liquidus silicate melts—is not completely understood. Experimental investigations in this field are certainly required although it is clear that simulating the conditions of open-system behaviour for Soret fractionation will represent a difficult experimental task.

Convection in magma bodies

There is one more issue that must be considered before the relevance of the Soret effect to the petrogenesis of basic–ultrabasic sills and layered intrusions can be justified—the nature of convection in magma

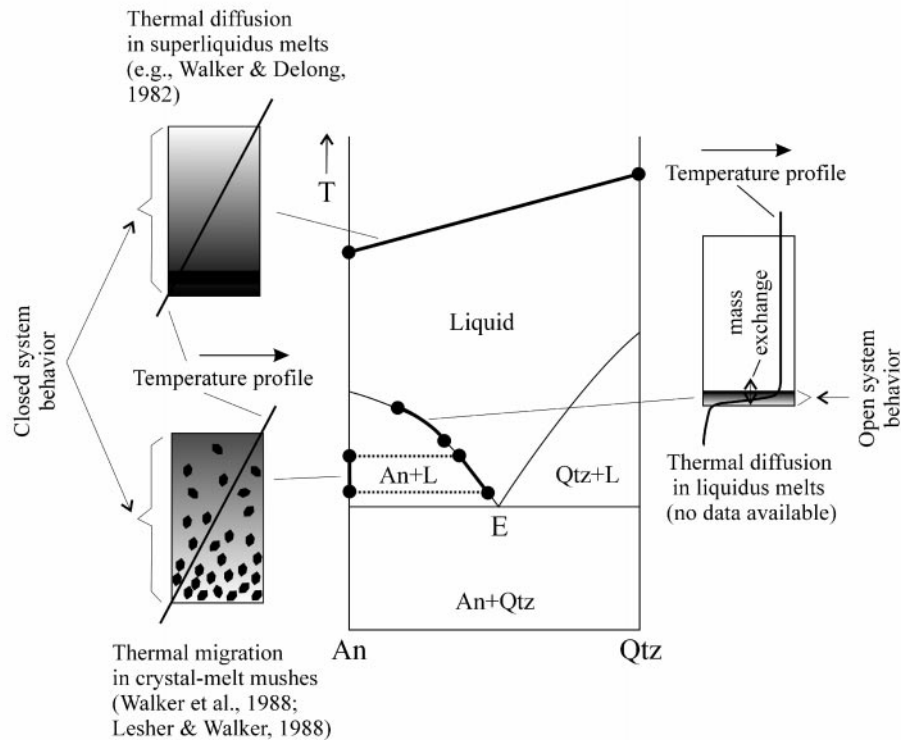


Fig. 12. The phase diagram An–Qtz schematically illustrating the gap in available experimental data on liquid fractionation in a temperature gradient. Experiments are limited to the study of thermal diffusion in superliquidus silicate melts and thermal migration in liquidus–solidus crystal–melt mushes. The process of thermal diffusion in liquidus silicate melts is not covered by experimental investigations. It should be noted that experiments on thermal diffusion are performed in conditions of a closed system when the entire charge, from the bottom to the top, is under a thermal gradient. In contrast, the simulation of the natural liquid boundary layer behaviour requires that only a small lower part of the charge is under a thermal gradient. In this case the liquid boundary layer can evolve as an open system exchanging matter with the overlying liquid that is kept under isothermal conditions. E, binary eutectic.

chambers. Soret fractionation can produce petrologically significant results only if the magma in the chamber experiences vigorous thermal convection. Most theoretical and experimental analyses indicate that even for fairly thin basic sills, Rayleigh numbers will be high enough for the occurrence of vigorous thermal convection, which rapidly transmits cooling to the centre of the main magma body (e.g. Huppert & Sparks, 1980; Martin *et al.*, 1987; Jaupart & Tait, 1995). However, this picture has been recently challenged (Marsh, 1988, 1989, 1990; Mangan & Marsh, 1992; Gibb & Henderson, 1992) by suggestions that convection is weak or nonexistent in almost all magma chambers. Combined experimental and theoretical studies have been used to show that convection becomes non-turbulent or even ceases upon loss of superheat (Brandeis & Marsh, 1989; Hort *et al.*, 1999). Hot debates on this issue between Cambridge (Sparks, 1990; Huppert & Turner, 1991) and Johns Hopkins University researchers (Marsh, 1990, 1991) have not clarified the situation pertaining to convection in magma chambers. The key reason for this is that the ideas about thermal convection in natural magmas

are based mainly on calculations, not on any direct observations of magma itself (Marsh, 1990). It seems, therefore, that the potential to resolve this conflict of views with the help of numerical modelling and experiments on paraffin and water–isopropanol solutions that are far from the composition of natural magmas may have been already exhausted. In such a situation it appears reasonable to return to the original information recorded in the rocks themselves. Let us re-examine whether the observational data are consistent with theoretical predictions of models involving vigorous or weak convection.

The models appealing to vigorous convection predict that most solidification of phenocryst-free magma in the chamber takes place from the bottom upwards despite the fact that cooling occurs predominantly through the roof (e.g. Woster *et al.*, 1990). When the floor and roof sequences are preserved, both show the same trend of differentiation, with the floor sequence typically being 6–7 times thicker than the roof sequence (Jaupart & Tait, 1995) (Fig. 13a). It is possible that vigorous thermal convection can lead to a very high heat flow through the roof that hampers or

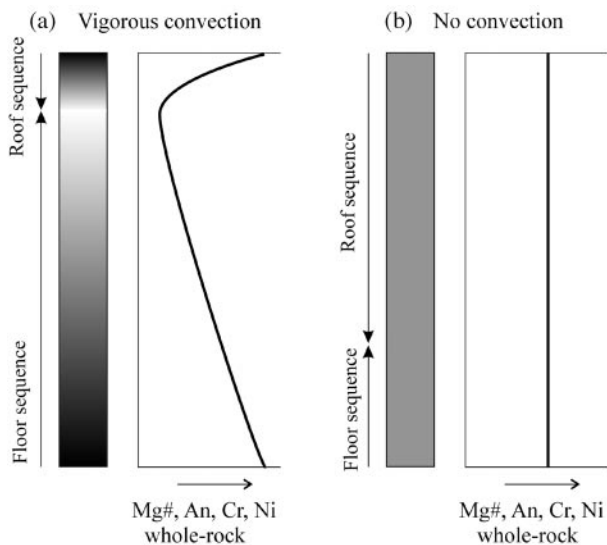


Fig. 13. Vertical sections and compositional profiles of sheet-like igneous bodies produced from phenocryst-free parental magmas as predicted by (a) crystallization models involving vigorous thermal convection in the chamber (e.g. Jaupart & Tait, 1995) and (b) crystallization models invoking weak or no thermal convection in the chamber (e.g. Marsh, 1996). In (a) the sill exhibits well-developed internal differentiation (highlighted by change in shading) in terms of whole-rock or mineral mg-number, An, Cr and Ni, with the floor sequence typically 6–7 times thicker than the roof sequence. In (b) the sill lacks internal differentiation, with the roof sequence significantly predominating over the floor sequence. (See text for further discussion.)

even completely prevents the formation of the roof rock sequence. In contrast, models invoking weak or no convection predict that most solidification of phenocryst-free magma in the chamber occurs from the roof downwards and consequently the roof sequences should be much thicker than those formed on the floor (Fig. 13b). The magma in the chamber is supposed to undergo very little, if any differentiation because all evolved liquids and newly formed crystals are captured within an upper solidification front (Marsh, 1988). It is also possible that crystal-laden plumes of material from a suspension zone in the upper solidification front can descend and deposit crystals on the lower front. In this case the floor sequence may become thicker than the roof sequence but the magma remains undifferentiated because crystals will be deposited constrained by the same phase equilibria, and this simply increases the volume of the lower front without causing any crystal fractionation (Marsh, 1996). In practice, this means that the identification of the floor and roof sequences will hardly be possible because of a lack of internal differentiation.

The critical test for the validity of convection or non-convection models can be provided by igneous bodies formed from initially phenocryst-free or phenocryst-

poor magmas. The bodies produced from such magmas are thought to possess so-called I-shaped compositional profiles showing no appreciable variations in SiO_2 and MgO content with stratigraphic height (Marsh, 1996). Three examples of such I-shaped profiles are discussed below. The first is the 50 m thick Ivanovskii sill on the Kola Peninsula, Russia (Sinitsin, 1965). The original section of the sill is nearly completely preserved, with only a few metres missing as a result of erosion of the upper contact (Fig. 14). The central portion of the sill reveals strikingly uniform variations in SiO_2 , MgO (not shown here) and CIPW normative composition, and can therefore be regarded as a typical example of an I-type sill formed from phenocryst-free parental magma. The phenocryst-poor character of the parental magma is also supported by petrographic observations (Sinitsin, 1965). The prominent increase in the grain size of the dolerites from the bottom upwards, progressive decrease in mg-number, Cr and Ni with height in the sill, and clear phase layering as seen in the successive appearance (pig, fa, qtz, fsp) and disappearance (opx, pig) of cumulus phases unambiguously indicate that the body crystallized from the bottom upwards. The proportion of the roof rock sequence, if it occurred at all, was relatively insignificant. Overall the body exhibits a very extensive differentiation sequence culminating with a granophyre-rich dolerite and granophyre at the roof of the sill. All these features of the Ivanovskii sill are in full accordance with predictions of convection models (Fig. 13a).

The second example is the 200 m thick New Mountain sill, Antarctica (Gunn, 1966), which is entirely composed of gabbro-norites and reveals a typical I-shaped profile in terms of SiO_2 and normative mineralogy (Latypov, 2003). A detailed study of the sill shows there are no phase changes with height in the sill, as augite, inverted pigeonite, plagioclase and chloritic micropegmatite occur throughout (Gunn, 1966). Continuous pegmatoid lenses occur ~30 m below the top of the sill. Despite the absence of any changes in silica content, the New Mountain sill exhibits a well-developed S-shaped cryptic profile in terms of mg-number, Cr and Ni, indicating that the body is fairly well differentiated. Also, the floor sequence is ~6–7 times thicker than the roof sequence, suggesting that the sill crystallized essentially from the bottom upwards. Thus the compositional profile of the New Mountain sill is in one-to-one correspondence to what is anticipated from convection models (Fig. 13a).

The third example is the 660 m thick Basistoppen sill emplaced as a single pulse of magma in the upper part of the Skaergaard intrusion, Greenland, and revealing little or no silica enrichment for at least 90% of the crystallization (Naslund, 1989). By this criterion the major portion of the sill is similar to I-type bodies.

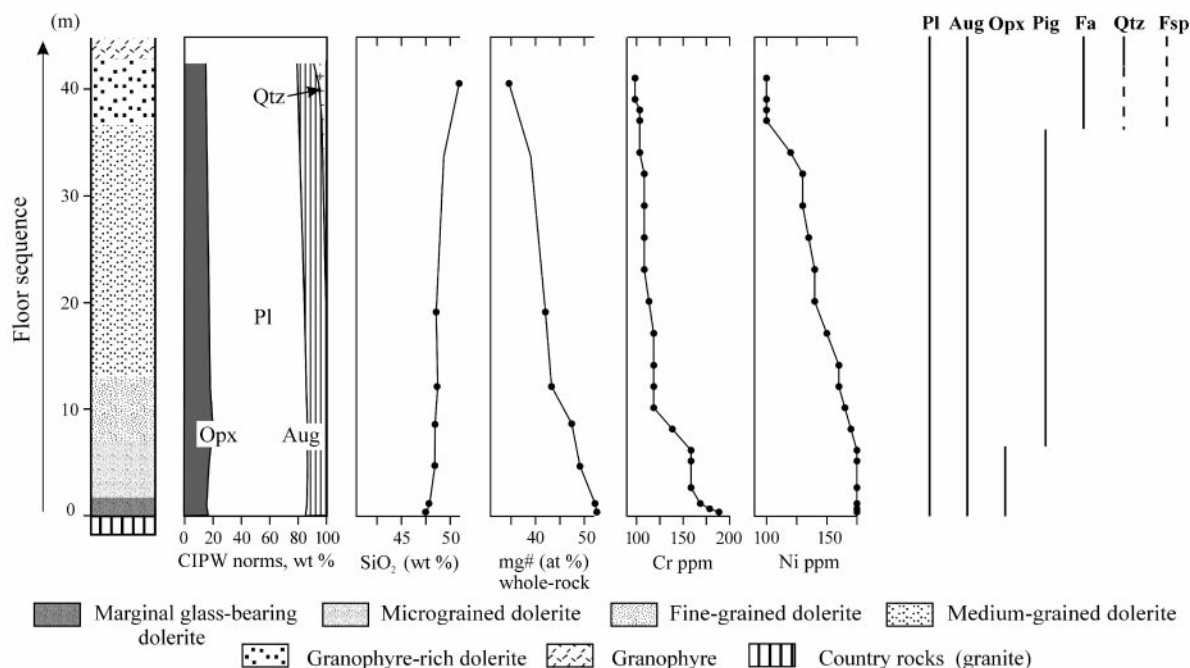


Fig. 14. Generalized stratigraphic section through the Ivanovskii sill (Kola Peninsula, Russia) showing variations in SiO_2 content and CIPW normative mineralogy compatible with I-shaped igneous bodies. Cryptic profiles in whole-rock mg-number, Cr and Ni contents with height indicate internal differentiation of the sill. The appearance (pig, fa, Qtz, Fsp) and disappearance (opx, pig) of cumulus (continuous lines) and intercumulus phases (dashed lines) along the section record progressive fractional crystallization. Phase and cryptic layering, as well as grain-size layering, in the dolerites indicates the crystallization of the sill from the bottom upwards. The original data for the figure are from Sinitin (1965). $\text{mg-number} = 100\text{Mg}/(\text{Mg} + \text{Fe}^{2+} + \text{Fe}^{3+})$.

The sill is composed of five major units (a gabbro picrite zone, a bronzite gabbro zone, a pigeonite gabbro zone, a fayalite gabbro zone, and a granophyre zone) recording the progressive fractional crystallization of the parental magma. A roof sequence is completely absent from the sill. Each zone is defined by the addition of a new cumulus phase or by temporary removal of olivine as a result of a resorptional reaction with the magma. These cumulus phases could not have been present when the magma was first intruded, strongly testifying to the absence of phenocrysts in the parental magma. The compositions of olivine, plagioclase and pyroxene change systematically from the bottom to the top of the sill, with the range of solid solutions comparable with those in the Skaergaard and Bushveld intrusions. These progressions in mineral compositions reflecting the internal changes in temperature and composition of magma in the chamber are in good agreement with predictions of convection models.

The first conclusion that can be drawn from the above data is that sheet-like bodies of uniform composition are probably rather rare or non-existent in nature. Our inability to recognize compositional zoning is a consequence of inappropriate choice of parameters of liquid differentiation rather than the absence of

differentiation itself. In particular, SiO_2 and MgO contents are poor indices of magmatic differentiation in magmas of roughly cotectic composition from which such I-type bodies as the Ivanovskii and New Mountain sills have been formed (Latypov, 2003). Whole-rock mg-number, the An content of plagioclase and compatible trace element abundances (e.g. Cr, Ni) are much more illustrative of differentiation in this particular case. I am inclined to believe that even the commonly cited example of an I-shaped igneous body, the Penneplain sill, Antarctica, will reveal clear signs of differentiation if the above indices are used instead of reported variations in SiO_2 , CaO, and MgO (Marsh, 1996). It is evident even from oxide variations that the Penneplain sill has a very well-developed marginal reversal exhibiting a clear progression from ~ 4 wt % MgO in the chilled margin towards 7 wt % MgO at a height of ~ 100 m (Marsh, 1996). This maximum is followed by a slight but steady decrease in MgO throughout a central portion of the sill down to 5 wt % at a height of ~ 300 m. These data are fully consistent with the observations of Gunn (1962), who found an increase in normative An from 61 to 67 in the marginal reversal and a clear decrease from 67 to 57 in the central portion of the Penneplain sill. There is therefore

little doubt that the crystallization of the Peneplain sill also occurred predominantly from the bottom upwards rather than in the opposite direction as predicted by non-convection models. It is also noteworthy that, in full accordance with predictions of convective models, the floor sequence of this sill is ~ 6 – 7 times thicker than the roof sequence.

The above examples of I-shaped sills provide clear evidence that most differentiation in sheet-like bodies filled with initially phenocryst-free magma takes place from the bottom upwards as predicted by models involving vigorous convection in the chamber (Jaupart & Tait, 1995). A non-convection model cannot explain the formation of highly differentiated bodies with clear predominance of the floor sequence over the roof sequence from initially phenocryst-free magmas. This implies that the basic principle of the model 'no phenocrysts, no differentiation' (Marsh, 1996) seems not to be supported by observation. The above conclusion is even further strengthened if data on layered intrusions are included. In particular, Sparks (1990) has clearly demonstrated that the predictions of a non-convection model are in striking contrast to actual observations on the Skaergaard intrusion. It can be shown that the same is true for most, if not all, basic–ultrabasic layered intrusions.

On the basis of the above analysis one can agree with the conclusion of Woster *et al.* (1990) that vigorous convection, significant internal cooling and differentiation can take place in a magma chamber even when there is no initial superheat. Most probably the kinetic undercooling at the interface of the mushy region of the natural roof with fluid magma provides Rayleigh numbers that are sufficient to drive thermal convection throughout the magma chamber (Woster *et al.*, 1993).

The above conclusion is strictly valid for relatively dry magmas, whereas it was concluded in the preceding sections that the parental magmas to basic sills and layered intrusions are predominantly water saturated. Although it is generally clear that the style of convection in the mafic melt has to be closely related to the volatile saturation, our knowledge on this matter is currently rather limited. The recent study by Cardoso & Woods (1999) has shown that in wet basaltic magmas, saturated with water, the production of small bubbles may dominate the density evolution of the mixture, causing a gradual decrease of the bulk density at the upper interface. Cool upper boundaries of the chamber may therefore become stable to convection. However, another regime of vigorous convection may develop as the bubbly mixture rises from cold lower boundaries. The intensity of such bubble-driven convection may be an order of magnitude greater than the purely thermal or compositional convection that arises in unsaturated melts (Cardoso & Woods, 1999). There

are, however, many uncertainties involved in the above analysis. In particular, consideration has been not given to the possibility of a continuous loss of a fluid phase through the roof rocks. This may probably result in the maintenance of the gravitational instability of the upper boundary layer and related vigorous convection even in the volatile-saturated magma. Clearly, further theoretical and experimental studies are urgently needed to provide more information about the possible styles and vigour of convection in water-saturated magmas.

SORET FRACTIONATION AS A MECHANISM FOR THE ORIGIN OF MARGINAL COMPOSITIONAL REVERSALS

The proposed compositional effects of thermal diffusion in liquid boundary layers permit the revival of the hypothesis of Soret fractionation and its application to explain the origin of marginal reversals. One possible scenario for the formation of a marginal compositional reversal is presented below.

The emplacement of fluid-saturated, phenocryst-poor, magma into cold country rock leads to the immediate formation of a fine-grained chilled margin, which will be close in composition to that of the initial magma. The great body of data on sills and layered intrusions indicates, however, that chilled or fine-grained rocks at the margins of these igneous bodies are not commonly consistent with the initial magma composition. The reason for this discrepancy most probably lies in the fact that the initial chilled margin is rarely preserved. As shown by Huppert & Sparks (1989), the initial chilled margin in most igneous bodies can survive for only a few tens of seconds.

As the conductive heat flux, F , in the wall rock decreases with time and heat flux, H , from the magma increases as the intrusion increases in thickness and convection is initiated (Fig. 15), the conductive heat flux in wall rock can eventually be exceeded by the heat flux from the magma. This eventually causes remelting and even the complete disappearance of the chilled margin that occurs at the first intersection of lines F and H (Fig. 15). For sills with thicknesses from 10 to 1000 m, the remelting of initial roof chilled margins of a few tens of centimetres to a few tens of metres in thickness is expected. Remelting of a chilled margin at the floor is considered to be less effective but can still occur by magma flow through the chamber of intrusion in which heat is advected to both boundaries (Huppert & Sparks, 1989). The common lack of mass balance between the floor chilled margins and the bulk composition of the intrusion can be taken as an

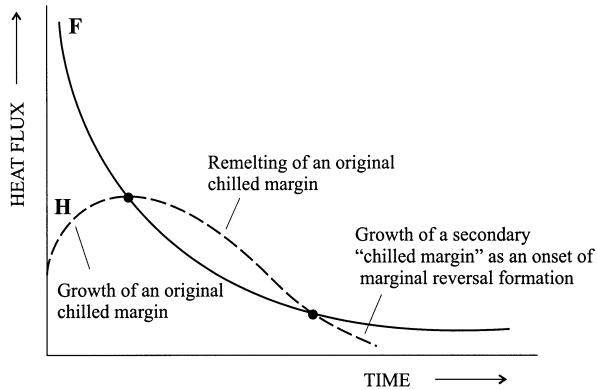


Fig. 15. Generalized variation of heat flux (H) in the melt and conductive heat flux (F) in the solid with time [slightly modified from Huppert & Sparks (1989)]. The heat flux in the melt is shown to follow a convex-up curve that intersects the concave conductive flux curve twice. An original chilled margin grows upon the first intersection of the heat melt flux and conductive flux curves, after which it starts to experience remelting up to complete disappearance. A secondary 'chilled margin' starts to grow at the second intersection of the melt heat and conductive flux curves. This point can be taken as an onset of marginal reversal formation.

indication that the marginal facies usually forms after prolonged meltback that destroys the initial chilled floor. With time convection wanes, and the heat flux from the magma once again declines to less than the conductive heat flux in the rock. At the second intersection of lines F and H (Fig. 15) a new generation of 'chilled margin' begins to grow, which I take as the onset of marginal reversal formation.

At this stage Soret fractionation starts operating effectively (Fig. 16a). The magma in the chamber vigorously convects, with convective velocities exceeding the settling velocities of the small amount of suspended phenocrysts (Huppert & Sparks, 1980). Vigorous magma convection in the chamber establishes a thin thermal boundary layer along the chamber margins, preventing the temperature contrast from dissipating. The boundary layer subjected to a temperature gradient is maintained out of equilibrium and tends toward a stationary non-equilibrium state, which is attained when the compositions and consequently the liquidus temperatures of the melts composing the boundary layers adjust to the imposed temperature gradient. To achieve such a compositional adjustment the system transfers HMPC (Ol components) of a parental magma X lying in the olivine field of the system $Ol-Pl-Cpx$ (Fig. 17b) from the liquid boundary layer into the main magma body whereas LMPC (components of the eutectic point E, $Ol + Pl + Cpx + L$) move in the opposite direction. Mass transfer across the short distance of the thermal boundary layer occurs by diffusion, aided by convection in the main magma body. Soret fractionation under the initial highest thermal

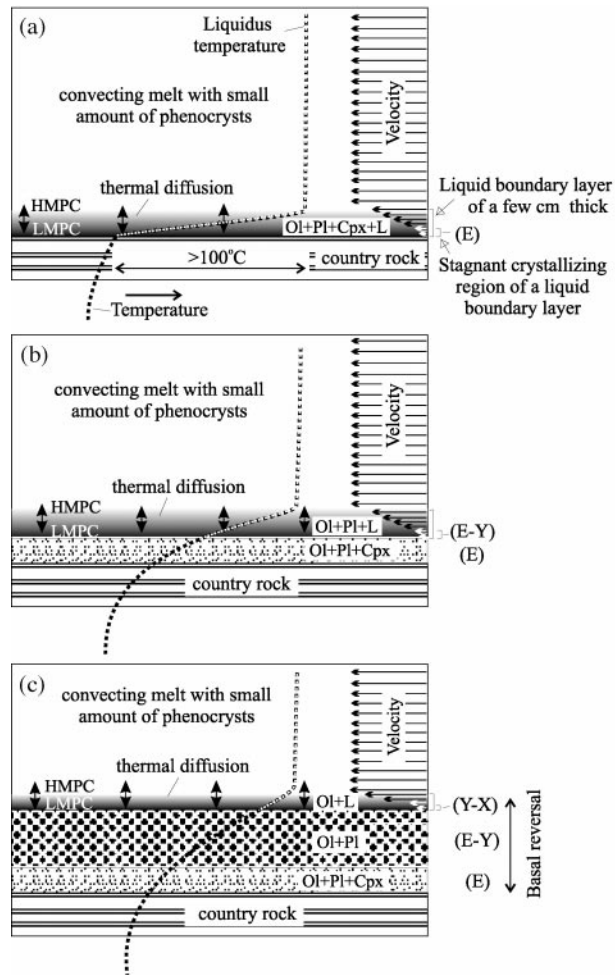


Fig. 16. (a–c) Successive stages in the course of formation of a marginal compositional reversal by Soret fractionation that produces liquid boundary layers in the sequence inverse to the normal trend of crystallization. The velocity gradient in the magma and thermal boundary layer prevents the temperature contrast from dissipating spatially near the edges even though the interior of the body cools and the magnitude of the thermal contrast decays with time. The thickness of the liquid boundary layer is greatly exaggerated for illustration purposes. The stages are designed for the initial liquid composition X lying in the olivine field of the system $Ol-Pl-Cpx$ (Fig. 17b). The abbreviations E, E–Y and Y–X refer to the phase diagram in Fig. 17b. The final rock sequence [olivine gabbro ($Ol + Pl + Cpx$), troctolite ($Ol + Pl$), dunite (Ol)] represents a mirror image of the future overlying Layered Series. (See text for further discussion.)

gradient (Fig. 16a) produces a liquid boundary layer comprising, in a stationary state, liquid compositions that span in reverse sequence a nearly entire liquid line of descent of the parental magma X. The uppermost liquid in this boundary layer corresponds to the parental magma of composition X, whereas the lowermost liquid is represented by the lowest-melting fraction of the initial parental magma, the eutectic liquid E ($Ol + Pl + Cpx + L$) (Fig. 17b). Compositional oversaturation in the main magma body arises as a result of

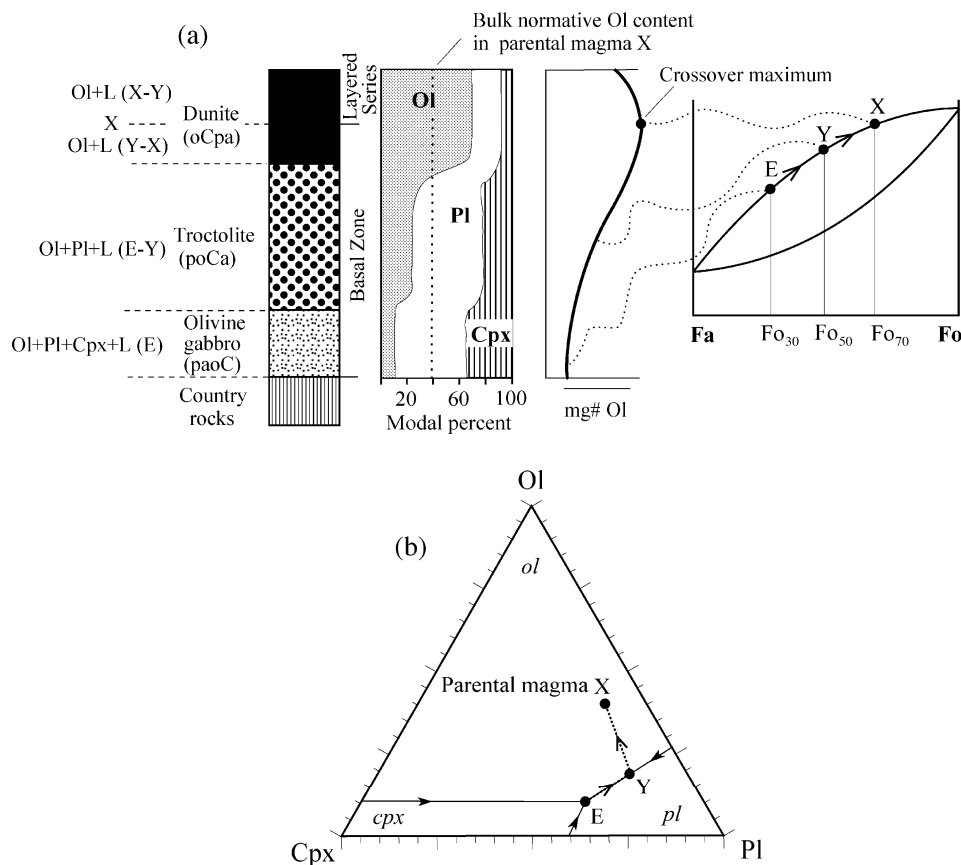


Fig. 17. The predicted compositional structure of a marginal reversal (a) for an initial liquid composition X lying in the olivine field of the system $Ol-Pl-Cpx$ (b). The marginal reversal shows an apparent lack of mass balance between the parental magma X and the lowermost rock of the sequence, olivine gabbro (paoC). It also displays an upward trend of phase differentiation $Ol + Pl + Cpx \rightarrow Ol + Pl \rightarrow Ol$ with roughly cotectic proportions of the crystallizing phases and reveals an upward mg-number enrichment trend. Both trends are opposite to that predicted from fractional crystallization of the parental magma X. The Fo–Fa phase diagram clarifies schematically the way in which such an mg-number enrichment trend can be produced by liquid differentiation along the inverse path $E \rightarrow Y \rightarrow X$. The extreme point X marks the upper boundary of the marginal compositional reversals and is referred to as the ‘crossover maximum’. (See text for further discussion.)

a supply of HMPC from the liquid boundary layer and is continuously balanced by corresponding growth of suspended phenocrysts in the convecting magma (Fig. 16) so that the magma throughout the chamber is maintained close to its liquidus.

Self-nucleation and crystallization predominantly occur in the stagnant region of the boundary layer adjacent to the front of the cumulus pile. The interface between solid and melt can be treated at this time as a flat boundary, such that there is a small gradient in the interstitial melt fraction below it. The first liquid to crystallize and to be incorporated into the consolidating cumulates in a stagnant region of the boundary layer will correspond to the eutectic liquid E. Crystallization at this point will proceed until the temperature in the stagnant region of the boundary layers above the growing cumulus pile is maintained at a level corresponding to this point. The crystallization of the

eutectic liquid E results in the formation of fine-grained olivine gabbro (pabC) directly at the contact with the country rock, despite the fact that the initial magma X in the interior lies in the primary olivine phase field. This explains why chilled or fine-grained margins in sills and layered intrusions are commonly much more evolved than the initial magma composition.

A further decrease in the magnitude of the thermal gradient in the boundary layer (Fig. 16b and c), related mainly to the formation of hot insulating cumulates and partly to the overall fall in the temperature of the entire magma body, will cause a gradual change in the composition of the liquids in the boundary layer. They will tend to become progressively more and more depleted in LMPC, shifting from the eutectic point $Ol + Pl + Cpx + L$ (Fig. 16a) along the cotectic line $Ol + Pl + L$ (Fig. 16b) and then into the primary field of olivine crystallization $Ol + L$ (Fig. 16c). In this way

the crystallization of the developing stagnant regions of the liquid boundary layer produces the compositional reversal spanning (in reverse order) the entire liquid line of descent of the initial parental magma X.

The final rock sequence (Fig. 17a) possesses all the properties of a typical natural marginal reversal, similar to those observed at the base of the Kharayelakh and Noril'sk-I sills (Figs 2 and 3). First, the rock sequence shows an apparent lack of mass balance between the chilled margin composed of olivine gabbro (paoC) and the bulk composition X. Second, it displays an upward phase differentiation trend $Ol + Pl + Cpx \rightarrow Ol + Pl \rightarrow Ol$ with roughly cotectic proportions of the crystallizing phases, which is opposite to that expected for fractional crystallization of the parental magma X. Third, it reveals an upward mg-number enrichment trend that is also opposite to that predicted by fractional crystallization of the parental magma X. The F_0 - F_a phase diagram (Fig. 17a) clarifies schematically the way in which such an mg-number enrichment trend can be produced by liquid evolution along the inverse path $E \rightarrow Y \rightarrow X$.

After reaching the parental magma composition X, the magma follows an evolutionary trend characterized by a decrease in mg-number, crystallizing along the normal path $X \rightarrow Y \rightarrow E$. The extreme point X, characterized by a maximum value of mg-number on the compositional trend, is referred to as the 'crossover maximum' and can be used to define the upper boundary of the marginal compositional reversals. A distinguishing feature of this crossover maximum is that the minerals and rocks here are characterized by the most primitive compositions observed in the whole intrusion. This boundary does not coincide with any lithological boundary, being located completely within the modally homogeneous dunite unit, and hence can be identified only by using mineral or rock chemical compositions. A more complex situation when the magma composition at the crossover maximum becomes more primitive than the parental magma composition is considered in a companion paper (Latypov, 2003).

At the level of the crossover maximum Soret fractionation becomes ineffective because the thermal gradient wanes in the liquid boundary layer. At this stage the transition from completely solid rock to the liquid interior will occur through a relatively thick crystal-liquid mush in which the interstitial liquid is considered to be convectively unstable in most cases (Jaupart & Tait, 1995; Tait & Jaupart, 1996). Once this instability occurs and vigorous exchange with the overlying chamber magma begins, the thin Soret-produced liquid boundary layer at the top of the mush is destroyed, and hence only the mushy layer mode of compositional convection remains. The further evolution of the magma in the chamber most

probably will proceed in conditions close to equilibrium. It is this change in the mode of magma differentiation that corresponds to the transition from the Basal Zone towards the overlying Layered Series in basic-ultrabasic sills and layered intrusions.

It follows from the above that the fundamental reason for the mirror relationship between the Basal Zones and Layered Series in many sills and layered intrusions is that they are produced under distinctly different thermodynamic conditions (Fig. 18). The Basal Zone forms through the liquid boundary layers developing in conditions of a stationary non-equilibrium state. In contrast, the Layered Series originates predominantly through the crystal-liquid boundary layers developing in conditions of equilibrium. Thus the importance of the crossover maximum is that it marks the boundary where a non-equilibrium style of evolution of the magma in the chamber gives way to the equilibrium style. The most important conclusion of the present study is that the mirror image of the marginal reversals results from the operation of non-equilibrium Soret fractionation, which works in a manner distinctly opposite to that of equilibrium crystal-liquid fractionation, which produces the Layered Series.

CONCLUSION

The most important conclusions of this study can be summarized as follows.

(1) Marginal compositional reversals representing, in terms of modal, phase and cryptic layering, a mirror image of the Layered Series are a remarkable and common feature of magmatic bodies irrespective of their size, form and parental magma composition. They have hitherto received little attention from petrologists. Deciphering the origin of marginal reversals can, however, contribute considerably to our understanding of the mechanisms of magma differentiation in crustal chambers.

(2) There are six distinctive features of marginal compositional reversals in basic-ultrabasic sills and layered intrusions that impose strict constraints on any model for their formation: (1) an apparent lack of mass balance between the lower part of the marginal reversals, including chilled margins, and the bulk composition of the intrusions; (2) phase crystallization sequences and (3) mineral compositional trends that are the inverse of those in the Layered Series; (4) the cotectic composition of rocks composing the marginal reversals; (5) the capacity to form from both phenocryst-rich and phenocryst-free parental magmas; (6) the capability to develop along the floor, subvertical walls and even the roof of magma chambers.

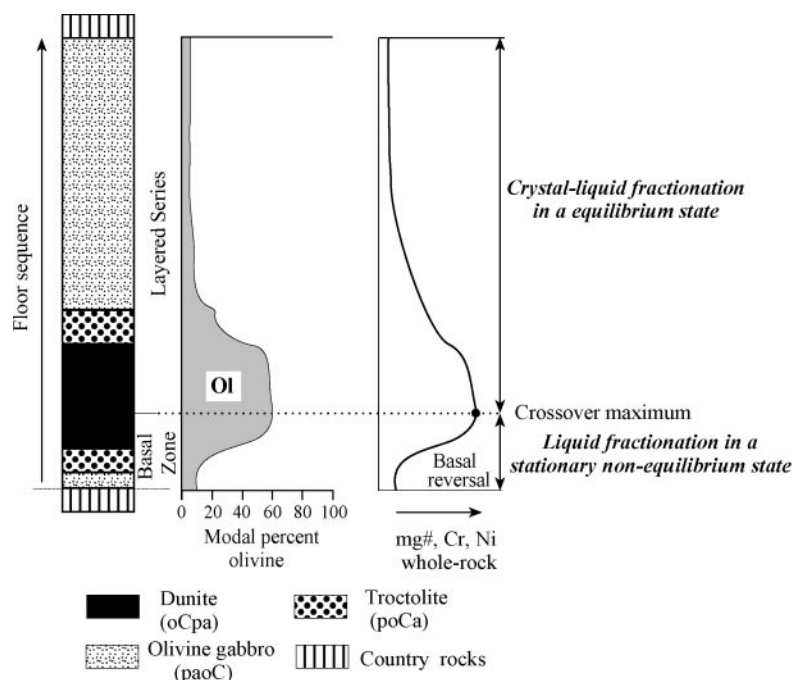


Fig. 18. Generalized stratigraphic section through a hypothetical intrusion composed of a Basal Zone and a Layered Series with variations in modal olivine and in whole-rock mg-number, Cr and Ni. The Basal Zone of the intrusion represents a well-developed compositional reversal characterized by an inverse order of phase crystallization $Ol + Pl + Cpx \rightarrow Ol + Pl \rightarrow Ol$, and a basal mg-number enrichment trend. The boundary between the Basal Zone and the Layered Series runs at the level of a crossover maximum. This level does not coincide with any lithological boundary, being located within the modally homogeneous dunite unit. The crossover maximum is distinguished by the most primitive compositions (mg-number) of the minerals and the bulk rocks observed in the whole intrusion. For the sake of simplicity the Top Zone and Upper Layered Series are absent from the intrusion. (See text for further discussion.)

(3) None of the current models of magma chamber evolution (e.g. crystal settling, continuous or multiple magma injection, flow differentiation, compositionally zoned magma, *in situ* crystallization) can provide an adequate explanation for the characteristic features of the marginal reversals.

(4) The process required to explain the origin of marginal reversals must be of universal character. It must be gravity independent, temperature gradient-driven and capable of producing a range of liquids spanning, in reverse sequence, the liquid line of descent of the parental phenocryst-poor magma at the floor, walls and roof of the magma chamber. The only currently known process that fully satisfies these criteria and can provide substantial chemical separation of initially homogeneous silicate liquids in a temperature gradient at the magma chamber margins is Soret diffusion.

(5) The main reasons why the Soret diffusion has so far been ignored as an agent of differentiation are that (a) chemical diffusion is considered to be a very slow process (10^{-5} – 10^{-9} cm^2/s) in essentially dry silicate melts compared with heat conduction (10^{-2} – 10^{-3}

cm^2/s), (b) the large temperature gradients at the chamber margins are difficult to maintain for a long time and (c) Soret chemical fractionation in experimental silicate liquids does not resemble that seen in any igneous rock suites. Also, the existence of vigorous convection within the main magma body that is required to develop thin thermal boundary layers along the chamber margins, thereby significantly reducing the Soret diffusion length scale, has been recently challenged (Marsh, 1988, 1989, 1990; Gibb & Henderson, 1992; Mangan & Marsh, 1992). The following suggestions have been made to overcome these obstacles.

(a) The problem of the slow chemical diffusion rate is resolved by the proposal that the magmas parental to most basic–ultrabasic intrusions are not dry but rather contain ~ 1 – 2 wt % H_2O and crystallized at a fluid pressure of < 1 – 1.5 kbar. This clearly follows from phase equilibria analysis showing that any ascending water-bearing basaltic magma can reach its liquidus and start to crystallize only after intersection with its vesiculation isopleth (Fyfe, 1970; Dubrovskii, 1984, 1993, 1998; Latypov, 2002). The idea is supported by

recent geochemical studies (Boudreau, 1992, 2002; Boudreau *et al.*, 1997). Compared with the dry basalts, the rate of chemical diffusion in H₂O-saturated basaltic melts is much higher; estimated to be in range of 10^{-4} – 10^{-5} cm²/s and 10^{-2} – 10^{-4} cm²/s for all non-alkali (e.g. Si, Al, Mg) and alkali (e.g. Na, K) magma components, respectively. It is also suggested that mass transfer in natural liquid boundary layers can effectively occur through the medium of a separate fluid phase that forms a continuous network of channels penetrating the layers. Because diffusivities of components through the aqueous fluids are very fast ($D = 10^{-2}$ – 10^{-4} cm²/s) and approach the diffusivity of heat (Watson, 1991; Watson & Wark, 1997), the combined mass transfer through the melt and fluid phase in the liquid boundary layers could probably result in a 'bulk' diffusivity of the order of 10^{-3} cm²/s. For such diffusivities the time required to achieve a Soret steady state in a 5 cm thick liquid boundary layer is only several hours. For the same time period and a rate of accumulation of 2–3 m/year, the cumulus pile will grow by <1 cm. Soret fractionation has therefore quite enough time to accomplish chemical separation in thin liquid boundary layers.

(b) On the basis of the results of Huppert & Sparks (1980), it is estimated that for small and medium-sized intrusive bodies (100–300 m thick) a temperature contrast decreasing with time from more than 100°C to a few degrees across a liquid boundary layer of a few centimetres thickness can be maintained over tens of years or more. In large layered intrusions a steady-state convective regime can be set up as a result of the prolonged filling of the magma chamber that could maintain a high thermal gradient at the margins during the juvenile stage of magma differentiation for thousands of years (Spera *et al.*, 1982). The persistence of the temperature gradient in the liquid boundary layers for such long time periods is quite sufficient to produce 10–100 m thick marginal reversals for reported rates of accumulation of marginal rocks in sills (2–3 m/year) and layered intrusions (1 m/year).

(c) The predictions of models suggesting weak or non-existent convection in magma chambers are found to be in striking contrast to the available data on compositional variations in basic–ultrabasic sills and layered intrusions. The occurrence of highly differentiated sills with I-shaped modal profiles, as well as differentiated bodies formed from initially phenocryst-free magmas but showing, nevertheless, a clear predominance of the floor sequence over the roof sequence, provides strong support for the suggestion that magmas in high-level intrusions are commonly in

a state of vigorous thermal convection (Huppert & Sparks, 1980; Martin *et al.*, 1987; Jaupart & Tait, 1995).

(d) The lack of convergence between the characteristics of chemical separation observed in Soret experiments and marginal compositional reversals is explained by the specific conditions of fractionation in natural liquid boundary layers. Unlike the experimental charges, natural liquid boundary layers evolve as open systems that exchange matter with the main magma body. As a result of this, Soret fractionation in natural, non-superheated, liquid boundary layers is controlled by liquidus phase equilibria even in the absence of a solid phase crystallizing. In contrast, liquid fractionation in Soret experiments takes place in a highly superheated region independent of phase equilibria constraints. For this reason the direct correlation of experimental results with natural observations is not justified.

(6) The key point for successful operation of Soret fractionation in nature is that, being subjected to temperature gradient, liquid boundary layers are maintained out of equilibrium with the tendency toward a stationary non-equilibrium state. The stationary state is attained when the compositions of the melts composing the boundary layers are adjusted to an imposed temperature gradient in accordance with liquidus phase equilibria. The compositional adjustment is carried out by transfer of high melting point components from the liquid boundary layer into the main magma body and low melting point components in the opposite direction. The required mass transfer is provided by Soret-induced diffusion across the thermal boundary layers, aided by vigorous natural convection in the main magma body. The first liquid boundary layer formed at the chamber margins comprises liquid compositions spanning nearly the entire liquid line of descent of the parental magma in reverse sequence. Nucleation and crystallization occur predominantly in the stagnant lowermost regions of the boundary layers composed of the most evolved liquid compositions. Upon progressive decrease in magnitude of the thermal gradient, related to the growing thickness of the cumulus pile and the overall fall in the temperature of the magma body, the compositional characteristics of the liquid boundary layers in the stationary state become more and more primitive. In this process the stagnant crystallizing region within the liquid boundary layer progressively travels all the way along the liquid line of descent of the parental magma. The formation of a marginal reversal can therefore be envisaged as a progressive

inward movement of a liquid boundary layer of a few centimetres thickness, the lowest, stagnant part of which is continuously consumed by the growing cumulus pile.

(7) Soret fractionation becomes ineffective and is overwhelmed by other processes, such as compositional convection in the mushy region of the crystal–liquid boundary layer, when the thermal gradient in the liquid boundary layer significantly diminishes. At this point, referred to as the ‘crossover maximum’, the formation of the Basal Zone under non-equilibrium conditions is inferred to give way to the formation of the Layered Series under equilibrium conditions. Thus the fundamental explanation for the mirror image of the marginal reversals is that non-equilibrium Soret fractionation works in a manner distinctly opposite to that of equilibrium crystal–liquid fractionation, which produces the Layered Series. The crossover maximum is distinguished by the most primitive compositions (high mg-number) of minerals and rocks observed within the intrusion. This boundary does not coincide with any lithological boundary and can be identified only by using mineral or rock chemical compositions.

(8) A clear advantage of the proposed model is that it accounts for nearly all the characteristic features of marginal reversals involving a single rapid or prolonged pulse of magma without appealing to any external or accidental processes such as wall-rock contamination, multiple magma injections, the amount of phenocrysts in the injected magma, the ability of newly formed crystals to settle to the bottom, crystallization along an inwardly inclined floor, etc. Work remains to be done, however, to establish the validity of the proposed model. First and foremost, further theoretical and experimental studies on thermal diffusion in open systems, especially those under near-liquidus temperatures and fluid-saturated conditions, are required, to make more accurate quantitative evaluation of the mechanism of Soret fractionation. This would help to put strict physical constraints on the proposed model for the origin of marginal compositional reversals. For specific examples of the application of the proposed Soret fractionation model the reader is referred to a companion paper (Latypov, 2003).

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